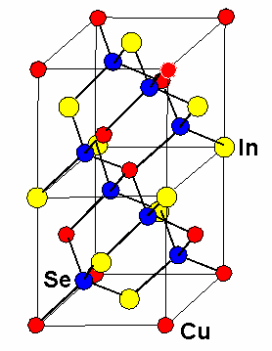
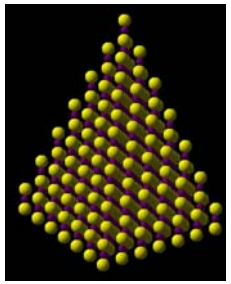
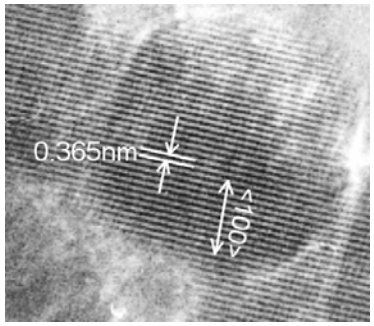
"Using Chemistry to Prepare New Better and Interesting Functional Materials"

Paul O'Brien

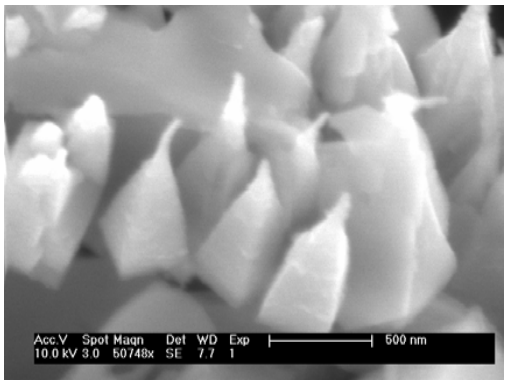




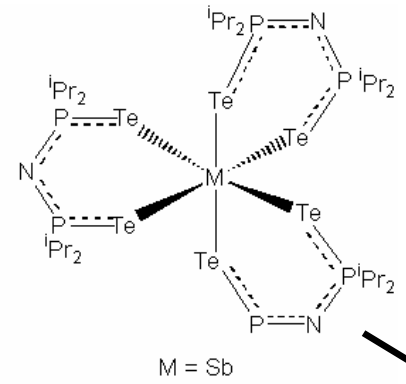
Professor of Inorganic Materials
in the Manchester Materials Science Centre and
the School of Chemistry,
University of Manchester,
Head School of Chemistry.

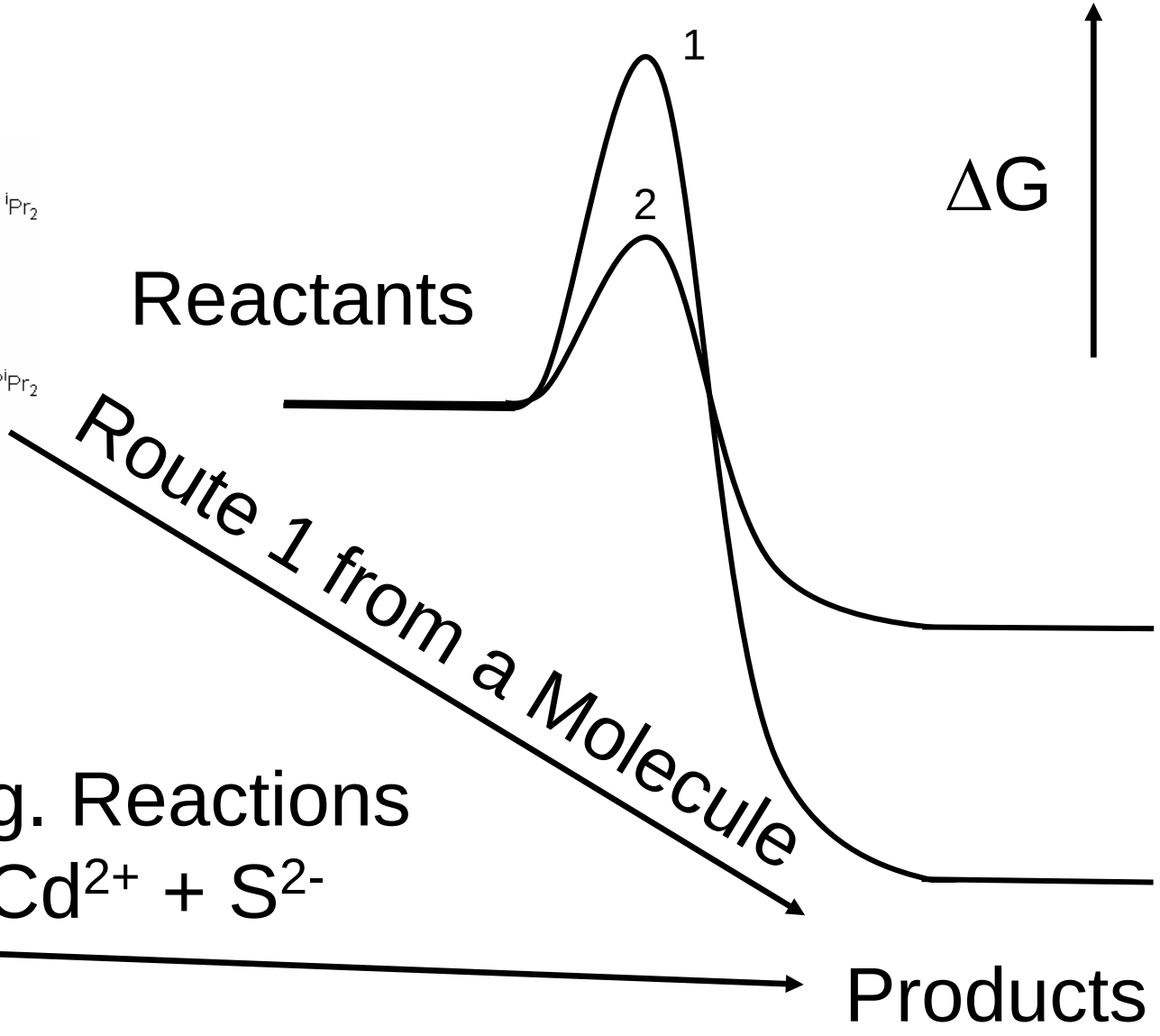


Workshop on Structure and Properties of Nanomaterials
A Partnership between
ICMR, Jackson State University and the University of Zululand
July 30-Aug. 2, 2007
at the Univeristy of Zululand



WE can think of 2 methods



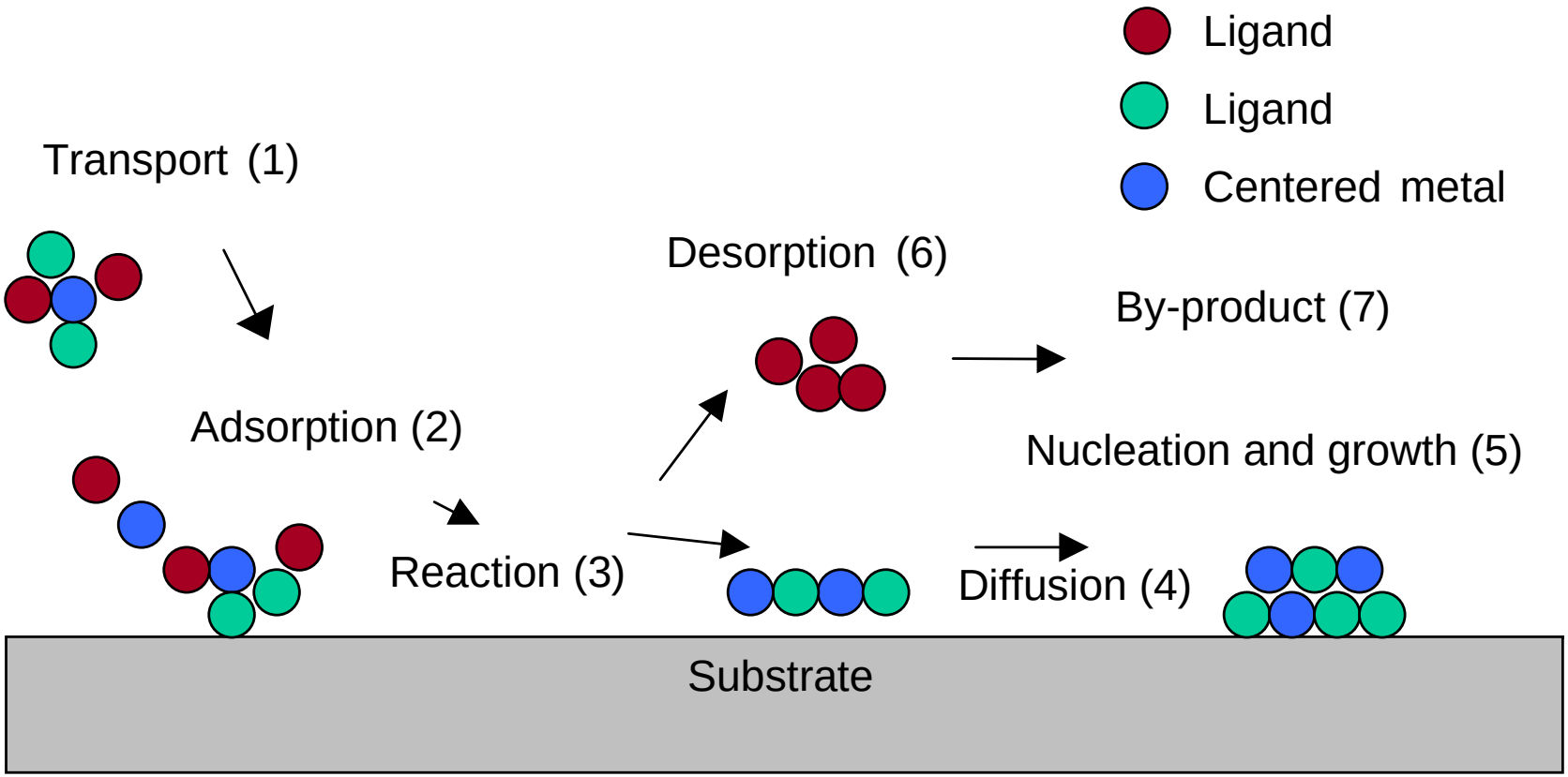


Plan for the Lecture

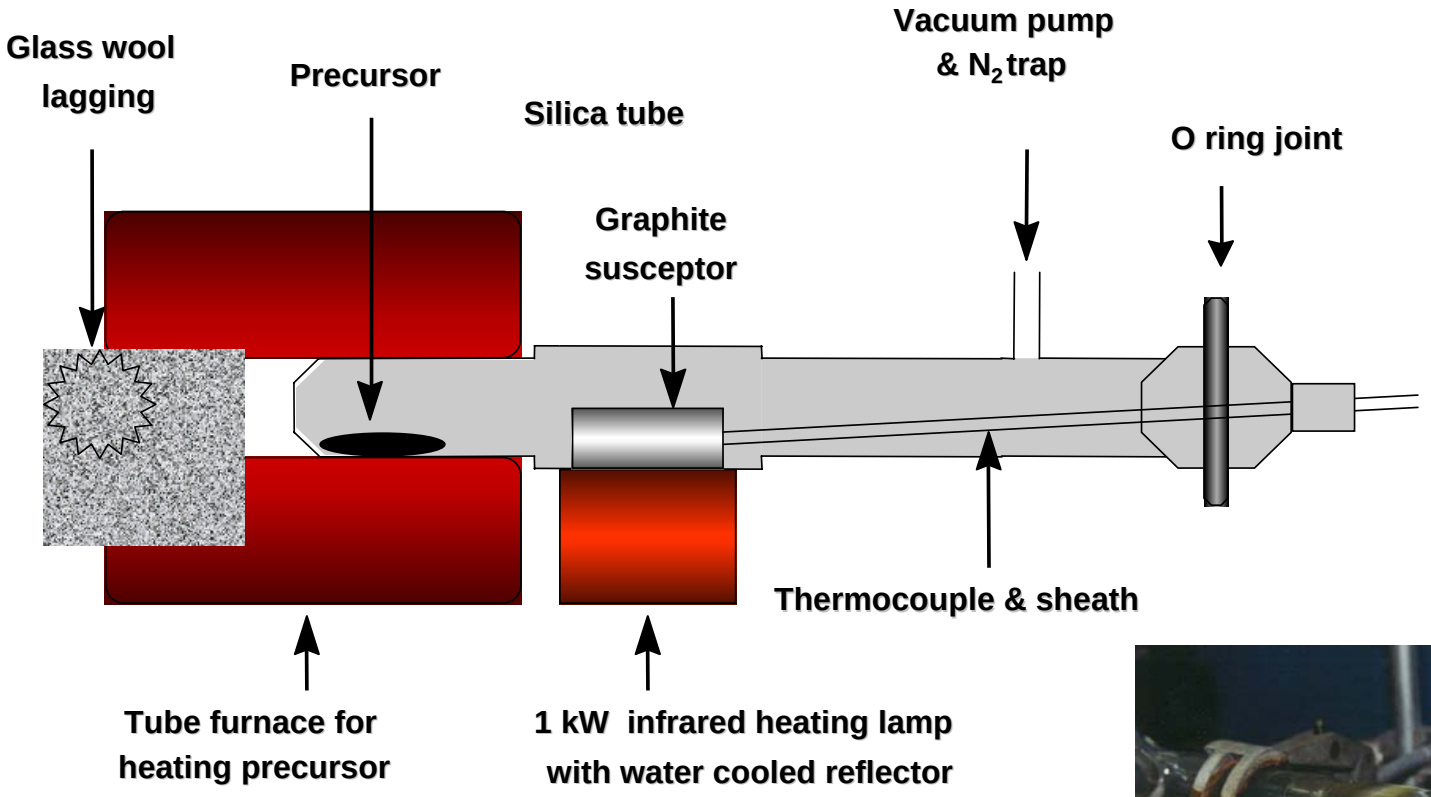
Build and Destroy!

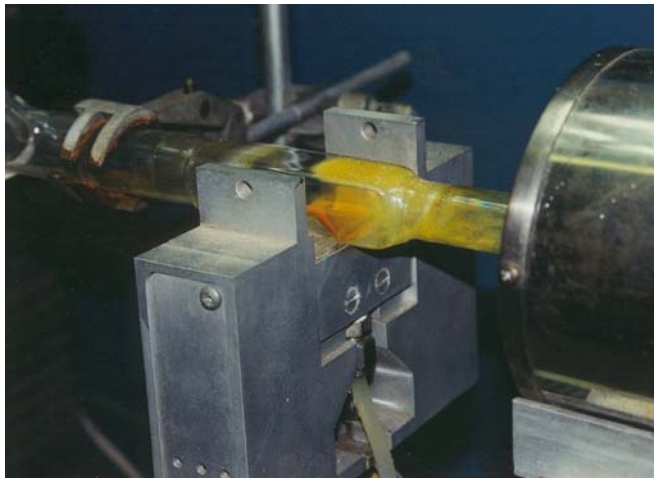
- **Dichalcogenoimidodiphosphinates**
- PbS
- New Composites-Utility?

The CVD Process

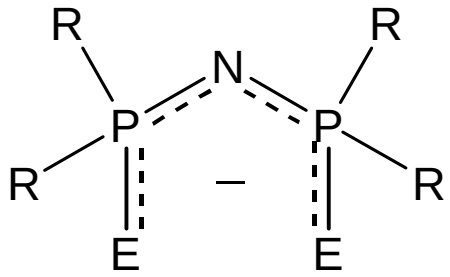


Low-pressure CVD





Dichalcogenoimidodiphosphinate Ligands



1 E = O
2 E = S
3 E = Se
4 E = Te

a R = Ph
b R = ^{i}Pr

$$Na[(P^{i}Pr_2)_2N] + Te \xrightarrow[Toluene]{TMEDA} (tmeda)Na[N(TeP^{i}Pr_2)_2]$$

a) A. Schmidpeter, H. Groeger, Z. Anorg. Allg. Chem.1966, 345, 106.

b) G. G. Briand, T. Chivers and M. Parvez, Angew. Chem. Int. Ed., 2002, 41, 3468.

c) M. Ellermann, M. Schtz, F. W. Heinemann, M. Moll, Z. Anorg. Allg. Chem. 1998, 624, 257.

d) D. Cupertino, D. J. Birdsall, A. M. Z. Slawin, J. D. Woollins, Inorg. Chim. Acta, 290, 1, 1999.

Synthesis of precursors

$NH(SiMe_3)_2 + 2{}^iPr_2PCl$

↓ Toluene

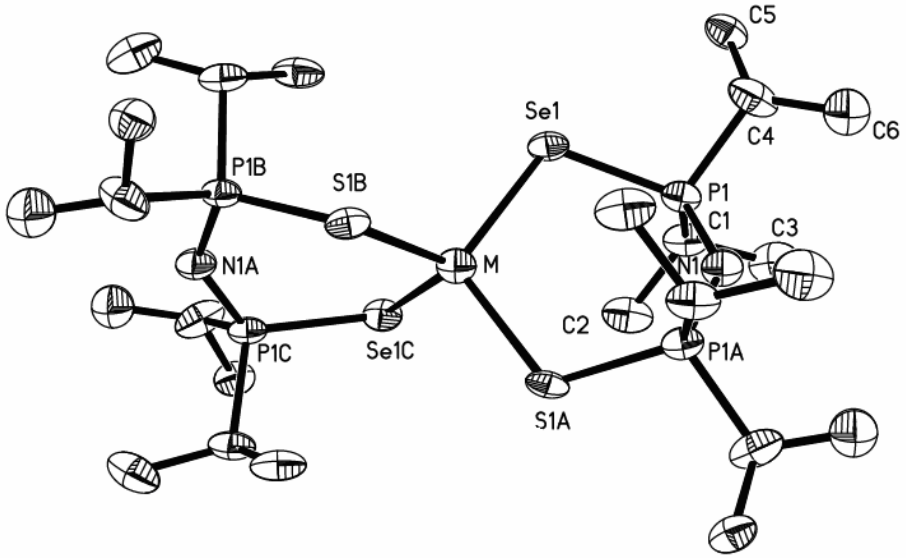
$^iPr_2PNHP^iPr_2 + 2SiMe_3Cl$

↓ **Se** **S**

$[^iPr_2P(S)NHP(Se)^iPr_2]^a$

$\frac{1}{2}\ CoCl_2.\ 6\ H_2O$ ↙ NaOMe ↘ $Ni(NO_3)_2.6\ H_2O$

$Co[^iPr_2P(Se)NP(S)^iPr_2]_2$ **$Ni[^iPr_2P(Se)NP(S)^iPr_2]_2$**



M = Co (or) Ni

cobalt(II) and nickel(II) iminobis (diisopropyl phosphine chalcogenide)

[a] J. D. Woollins *et al.*, *Inorg. Chim. Acta.*, 1999, **290**, 1

CVD studies of $Co[^iPr_2P(Se)NP(S)^iPr_2]_2$

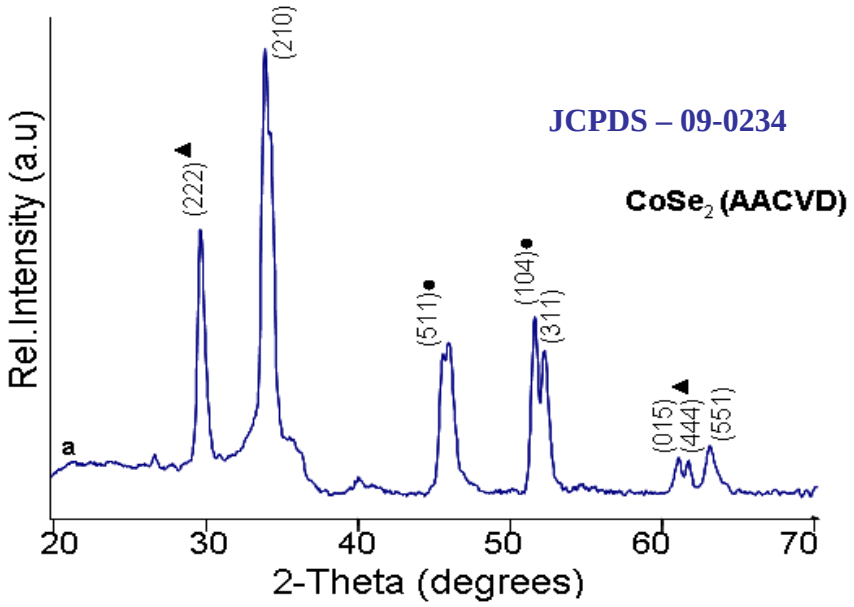
AACVD → **Cubic $CoSe_2$**

$Co[^iPr_2P(Se)NP(S)^iPr_2]_2$ — 475 – 425 °C Substrate temperature (T_{subs})

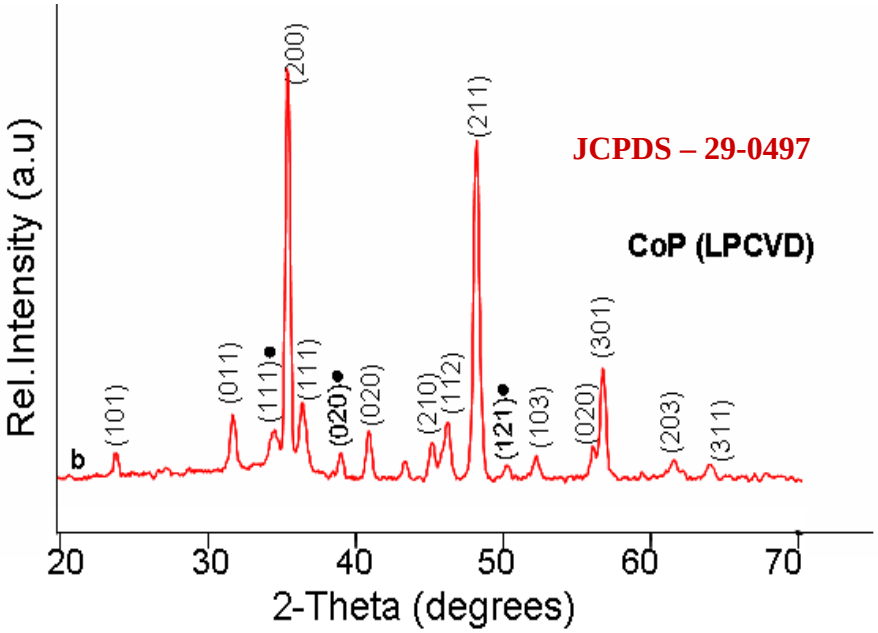
LPCVD → **Orthorhombic CoP**

T_{subs} -475 – 375 °C

Precursor temperature T_{prec} -300 °C.



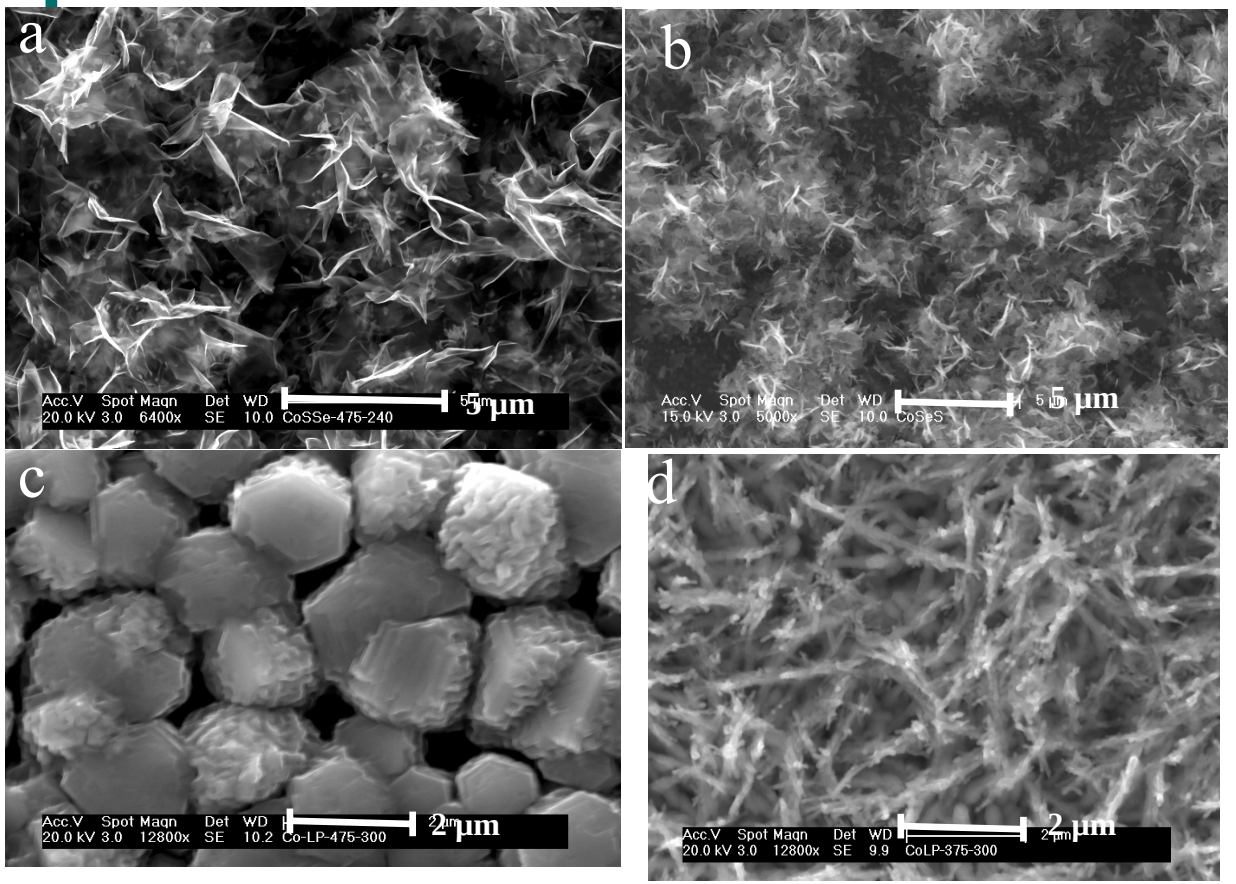
▲Co_9Se_8 , (●) P



(●) P

SEM of cobalt selenide and cobalt phosphide films

$CoSe_2$ - 475 °C
AACVD

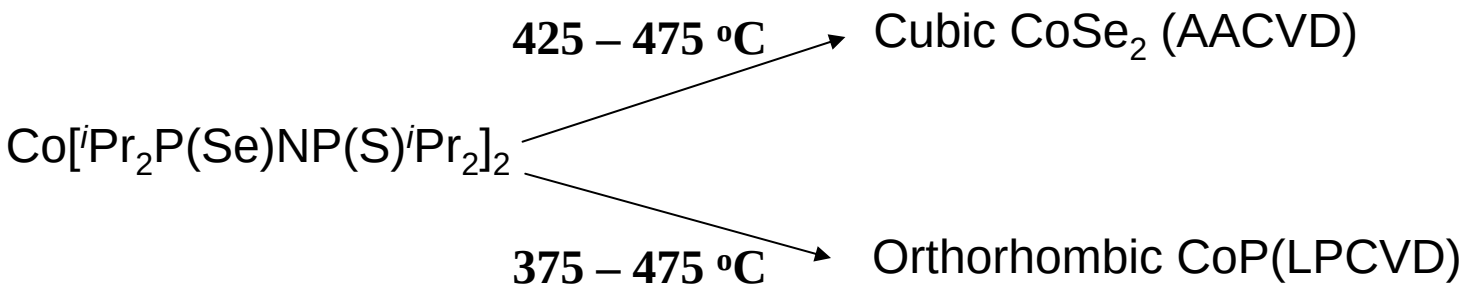


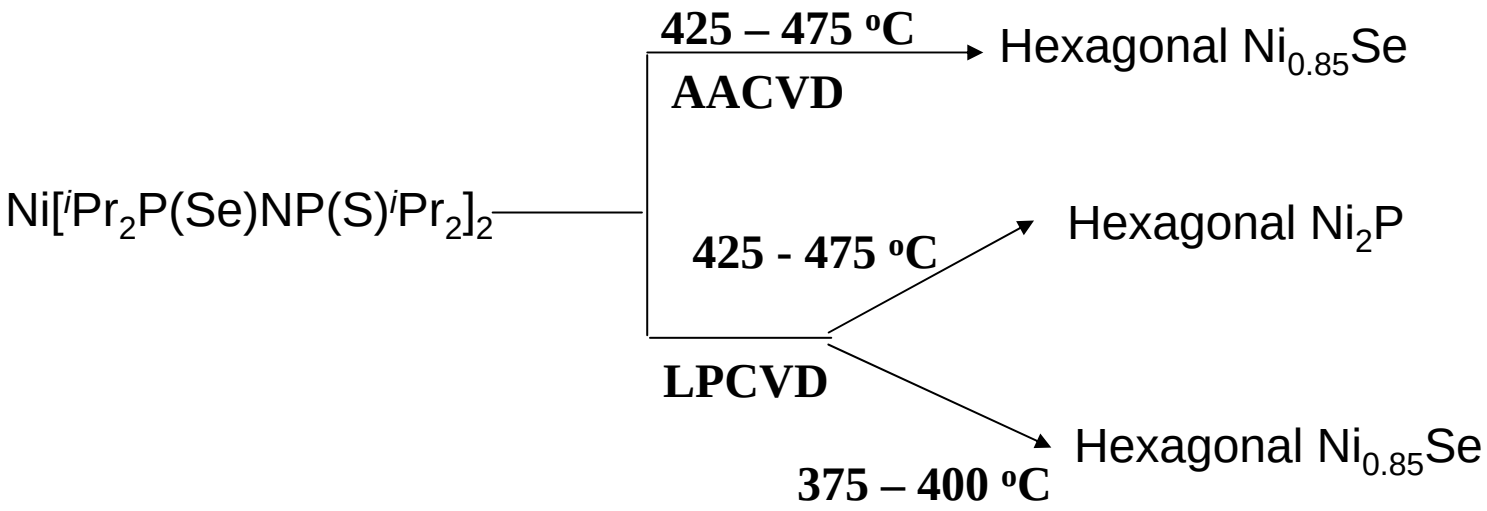
$CoSe_2$ - 425 °C
AACVD

CoP, T_{subs} = 475 °C,
T_{prec} = 300 °C, LPCVD

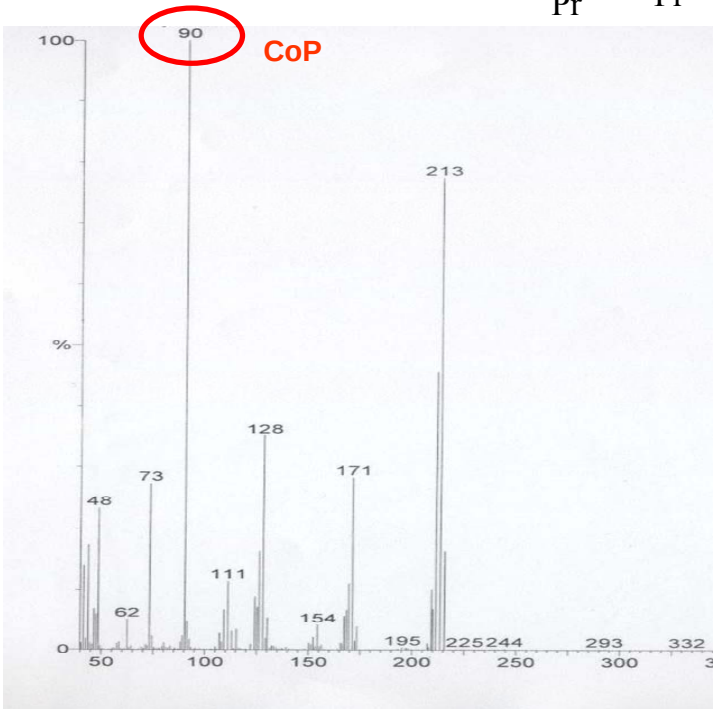
CoP, T_{subs} = 375 °C
T_{prec} = 300 °C, LPCVD

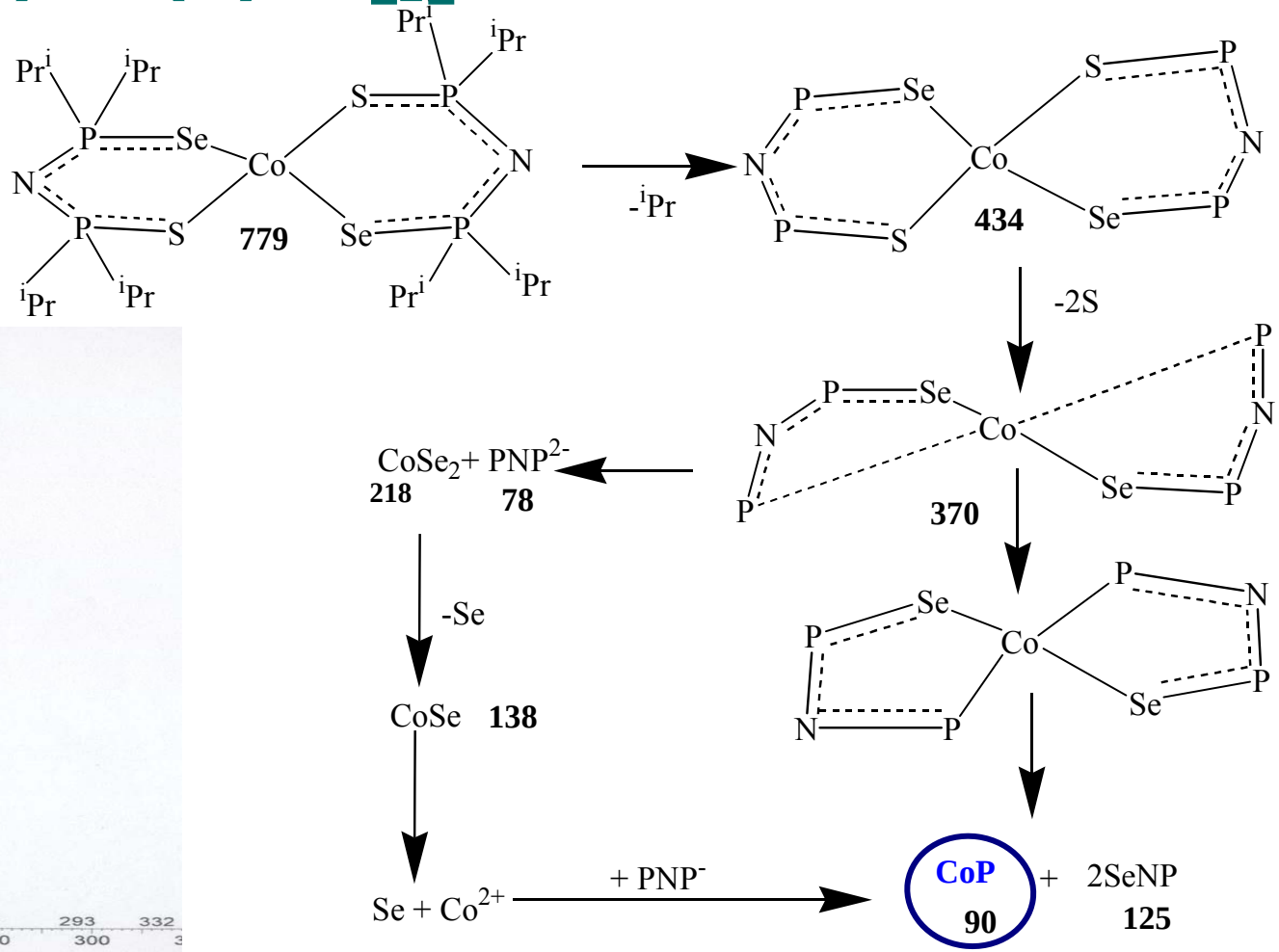
Summary of CVD studies of M[^{i}Pr$_2$P(Se)NP(S)^{i}Pr$_2$]$_2$





Pyrolysis GC-MS studies of $Co[^iPr_2P(Se)NP(S)^iPr_2]_2$





iPr = isopropyl

$$Na[(P^iPr_2)_2N] + 2Te \xrightarrow[TMEDA]{\text{Hot Toluene}} (tmeda)\,Na[N(TeP^iPr_2)_2]$$

$$MX_2 + 2\,(tmeda)Na[N(TeP^iPr_2)_2] \xrightarrow[-2\,NaX,\ -tmeda]{\text{Diethyl ether}} M[(TeP^iPr_2)_2N]_2$$

M = Cd (**1**), X = I; M = Hg (**2**), X = Cl, tmeda = tetramethylethanediamine

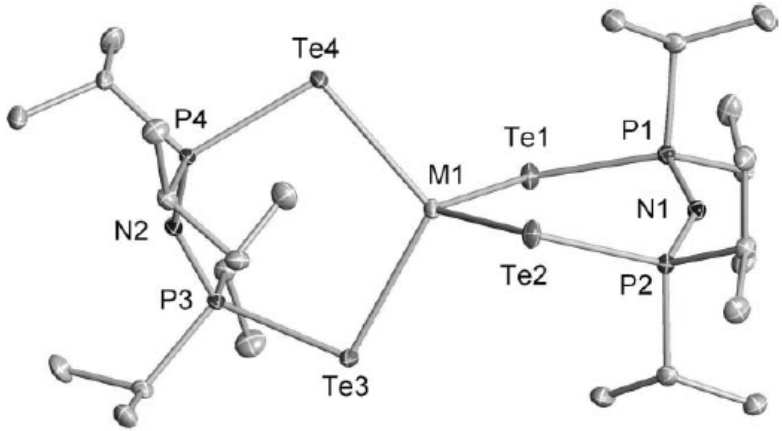


Fig. 1 Thermal ellipsoid plot (30% probability) of the structure of **2a** (M = Zn), **2b** (M = Cd) and **2c** (M = Hg). Hydrogen atoms have been omitted for clarity.

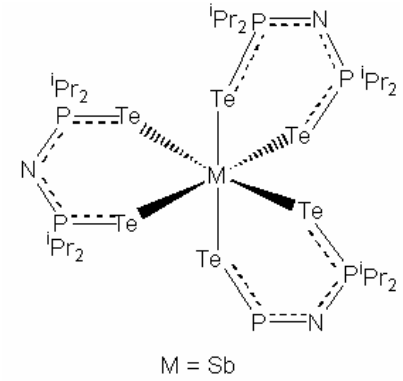
Synthesis and structures of M[N(TePPr$^i_2$)$_2$-*Te*,*Te*′]$_n$ (*n* = 2, M = Zn, Cd, Hg; *n* = 3, M = Sb, Bi): the first ditelluroimidodiphosphinato p- and d-block metal complexes

Tristram Chivers,* Dana J. Eisler and Jamie S. Ritch

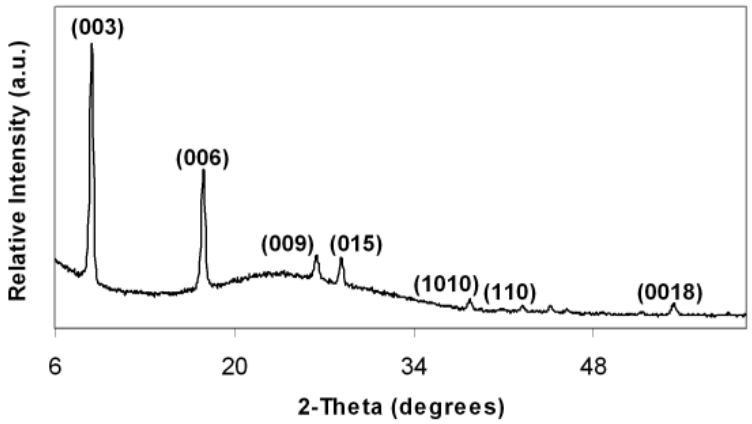
Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4. E-mail: chivers@ucalgary.ca; Fax: (+1)403-289-9488; Tel: (+1)403-220-5741

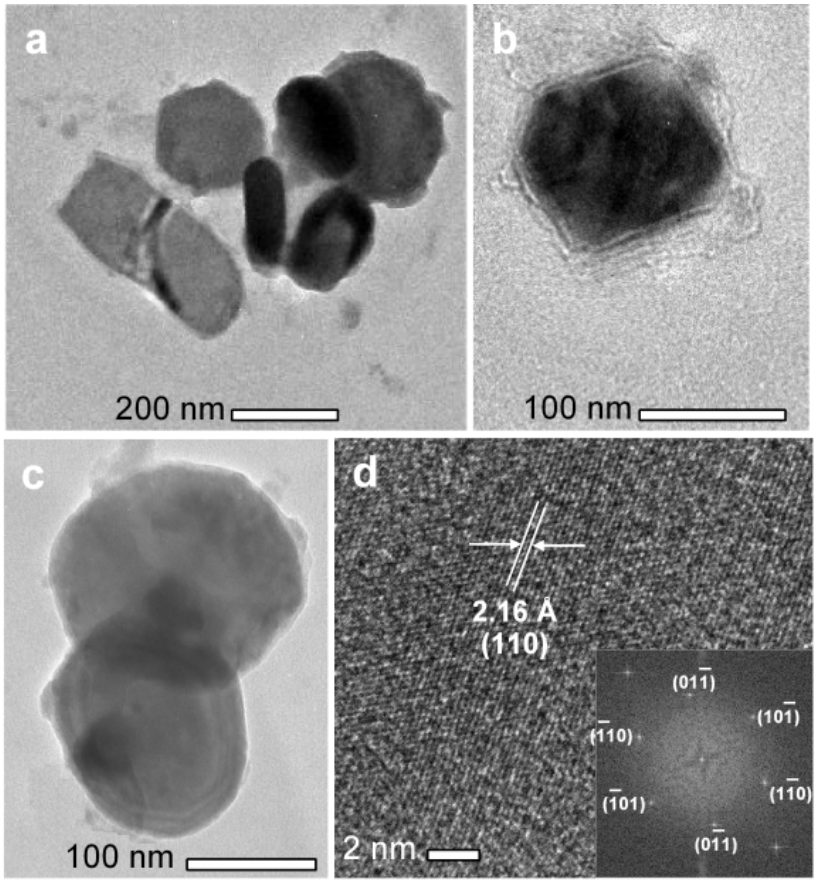
AACVD studies of $Sb[(TeP^{i}Pr_2)_2N]_3$

• pXRD of rhombohedral Sb_2Te_3 thin films at 475 ^{o}C with a dynamic argon flow rate of 240 sccm.



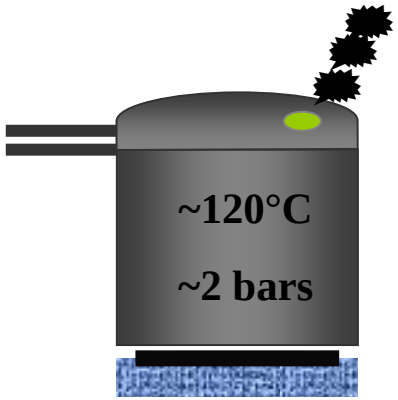
475 ^{o}C





S. S. Garje, D. J. Eisler, J. S. Ritch, M. Afzaal, P. O'Brien, and T. Chivers, J. Am. Chem. Soc, 2006, 128, 3120.

SOFT HYDROTHERMAL ROUTE



- Standard pressure-cooker
- Soft conditions allowing:
  - Very low amount of waste
  - Highly crystalline particles

In a typical experiment, an aqueous suspension containing the precursor metal complex and the surfactant was prepared.

Decomposition of the precursor was achieved using a household pressure-cooker.

INTRODUCTION

- **Strong quantum confinement effect**

  Exciton Bohr Radius:α_B=20nm

  Bulk band gap: Eg=0.41eV

- **Wide range of applications**

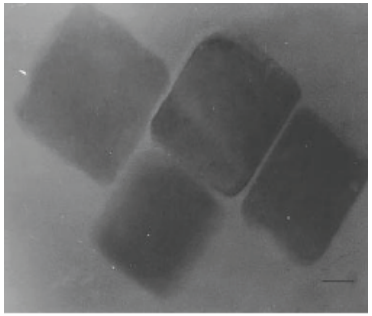
Telecommunication and biological applications: NIR luminescence (1300–1550 nm and 700–900 nm)

Optical switching and photonic devices: NLO behavior within the confinement regime is expected to be significantly greater than for II–VI materials

PREVIOUS WORK

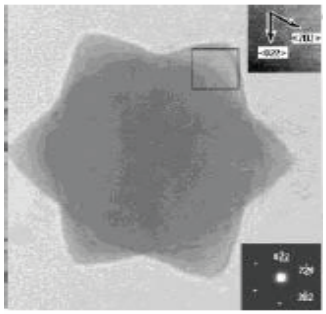
Single Source Precursor

$Pb(S_2CNEtPr^i)_2$ in TOPO



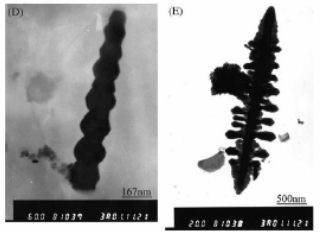
O'Brien et al., J. Mater. Chem. 1997

$Pb(S_2CNEt_2)_2$ in phenyl ether and dodecanethiol

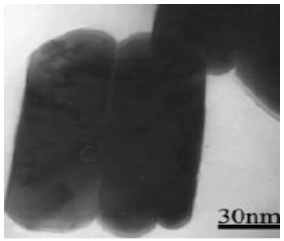


Sheon et al., J.Am Chem.Soc. 2002

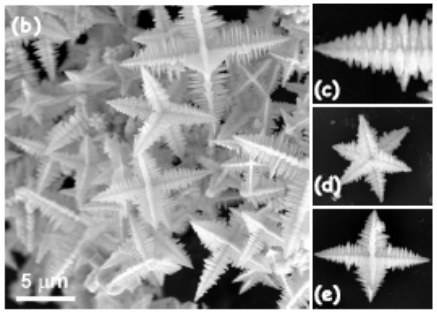
Solvothermal/Hydrothermal



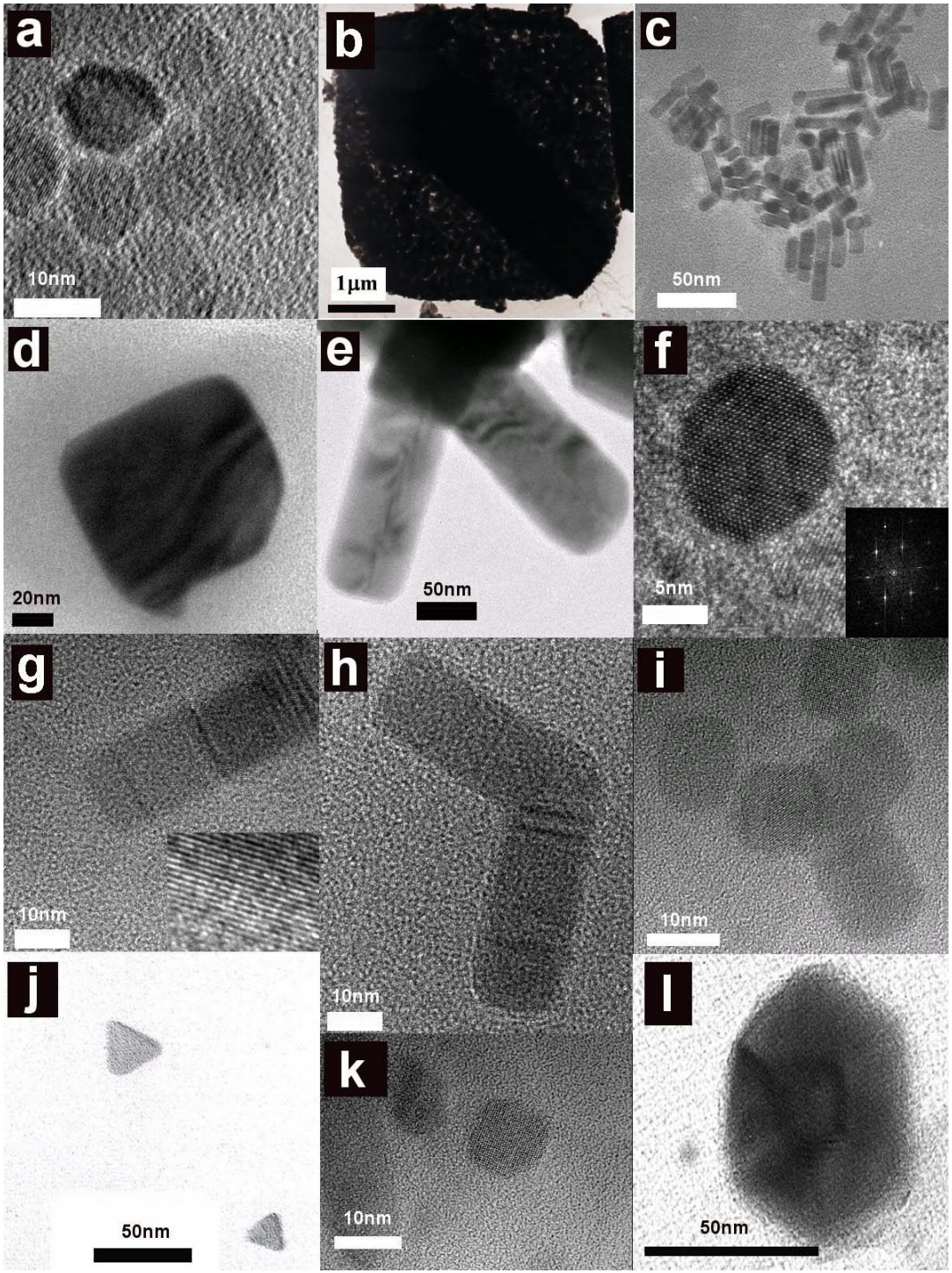
M.-s. Mo et al. Journal of Crystal Growth 2002



Wang et al. J. Phys. Chem. 2006



Komarneni et al., Nanotechnology 2006



The precursors chosen in this work

(**A**: [2,2' bipy-($Pb(SC(O)(C_6H_5)_2)$];

B: [$Pb(S_2(P(C_6H_5)_2)_2N)$]);

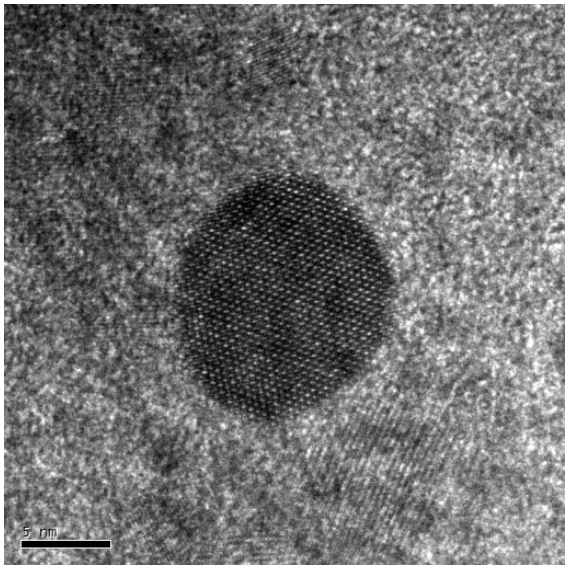
C: [2,2'-bipy($Cd(SC(O)(C_6H_5)_2)$])

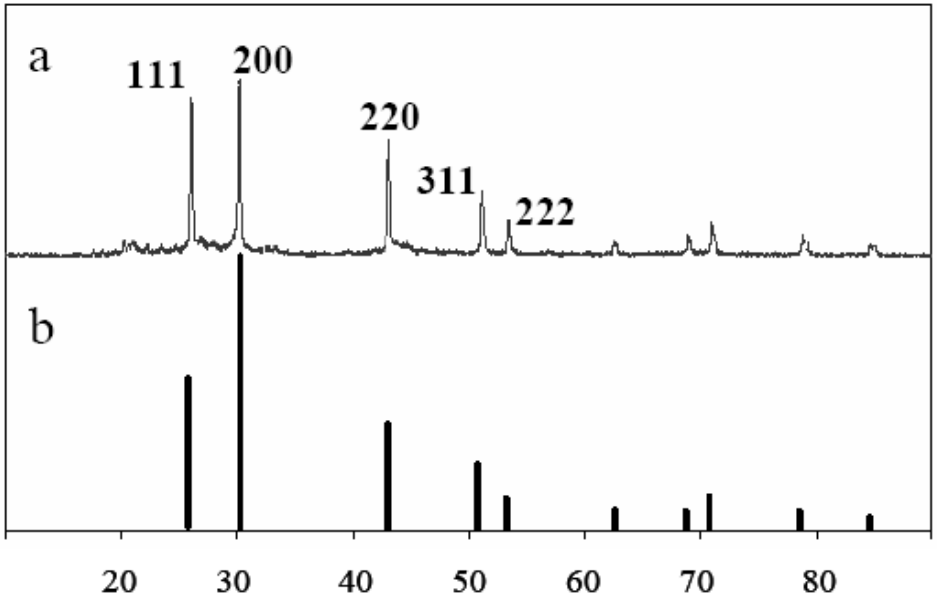
TEM images obtained for PbS nanocrystals grown using precursor

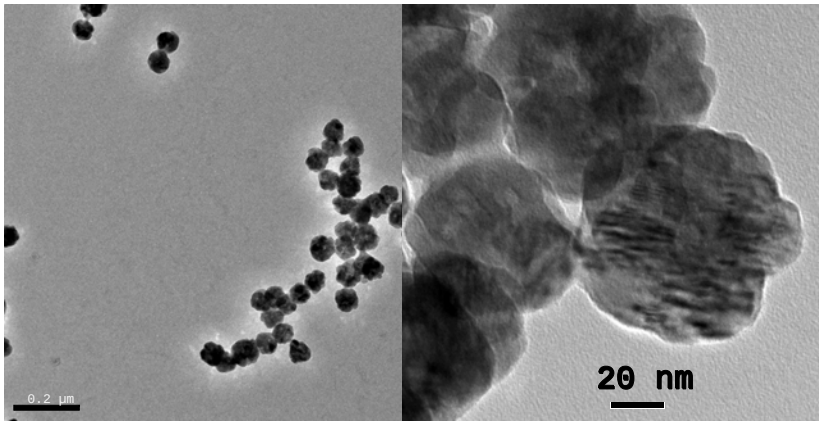
A (a-g) and

B (h-l)

[(2,2'-bipyridyl)Pb(SC{O}(C_6H_5))$_2$]



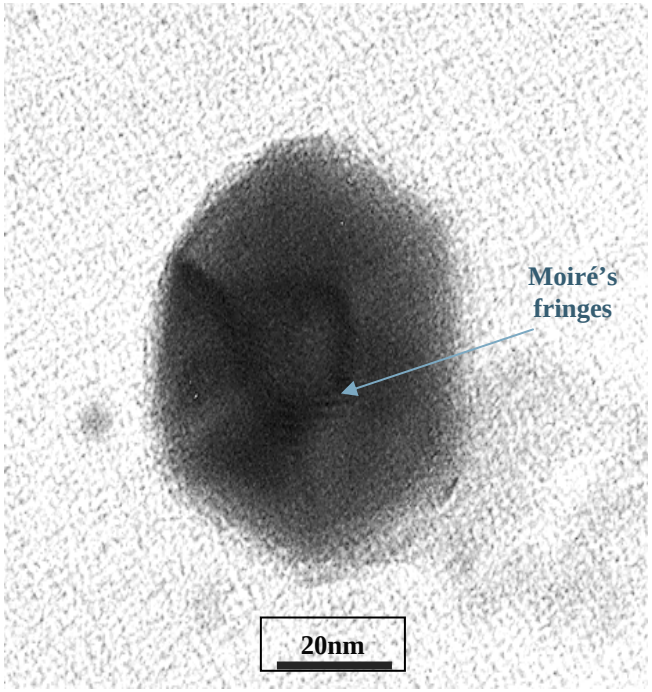




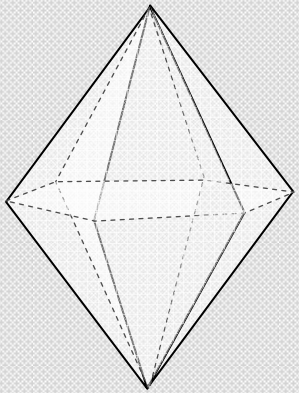
Increased reaction time

Representative powder XRD of PbS nanocrystallites

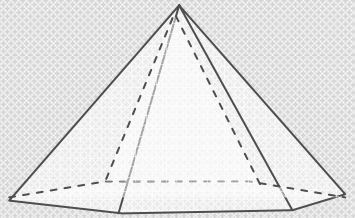
Chem. Comm. 2006, 4709–4711



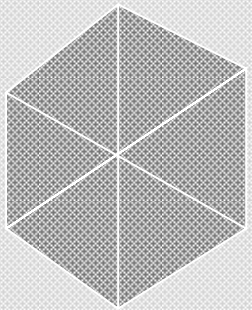
Hexagonal bipyramide



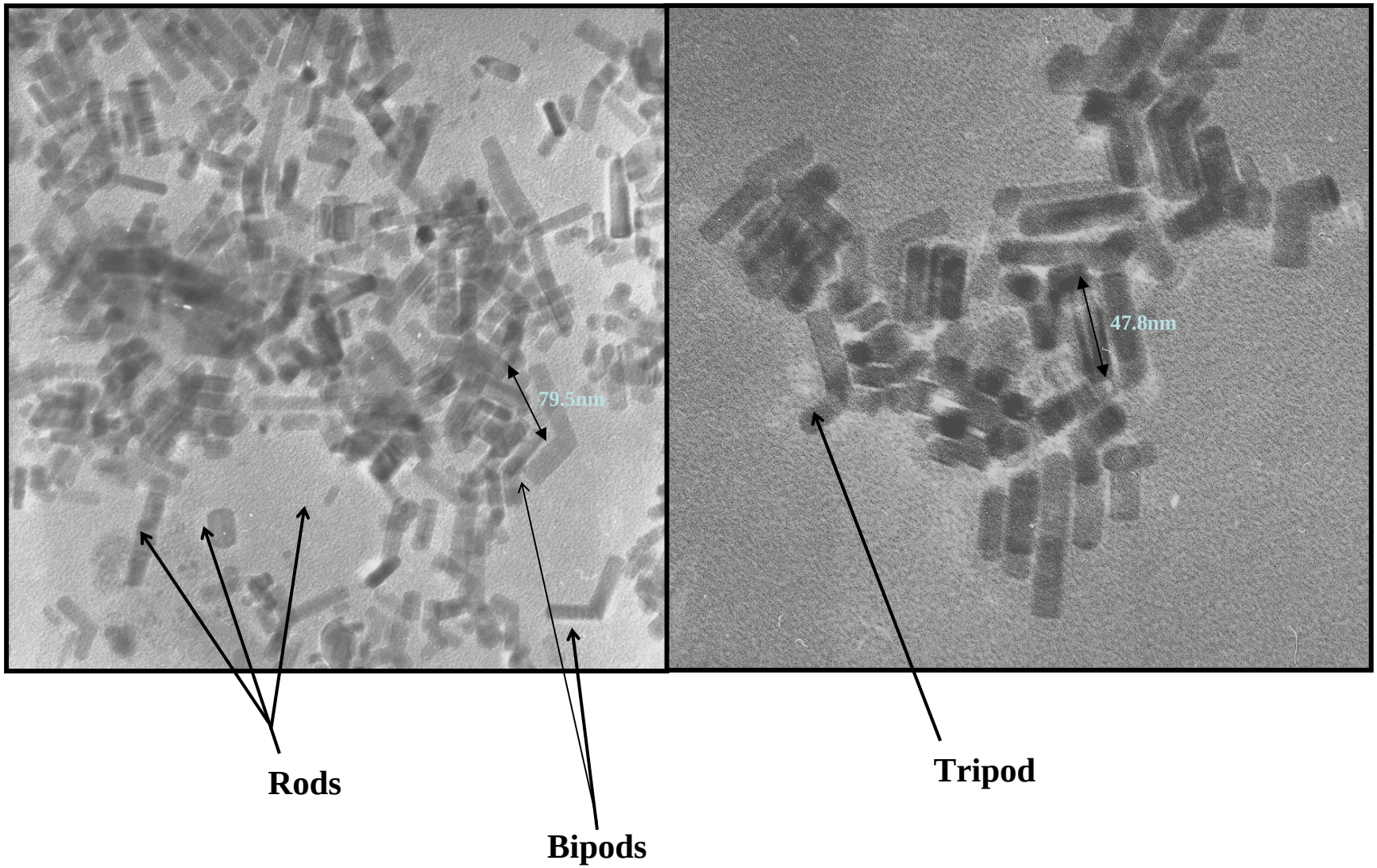
Hexagonal pyramide

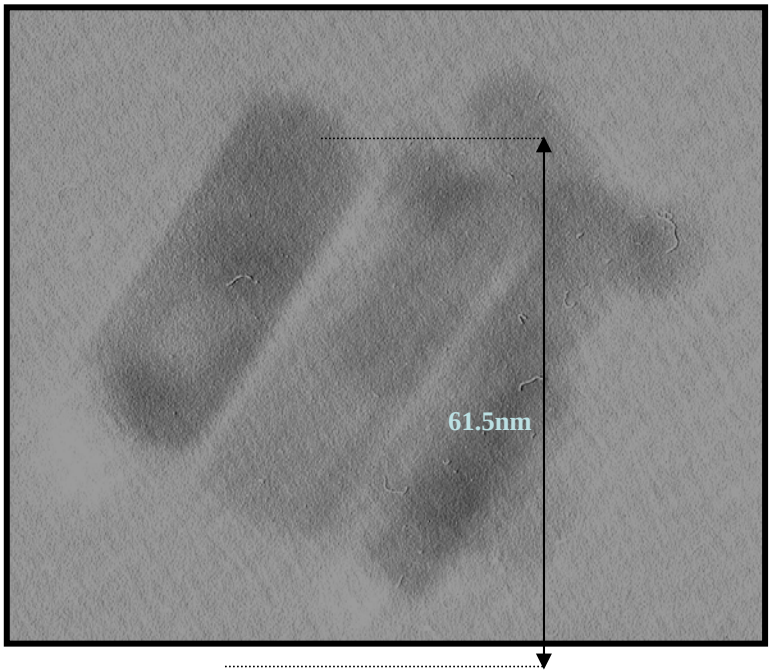


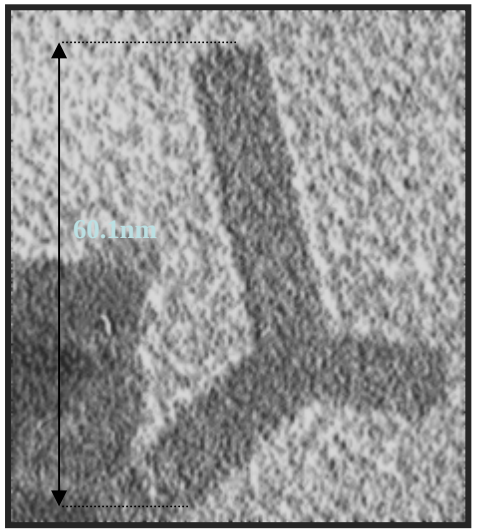
➔Seen from above

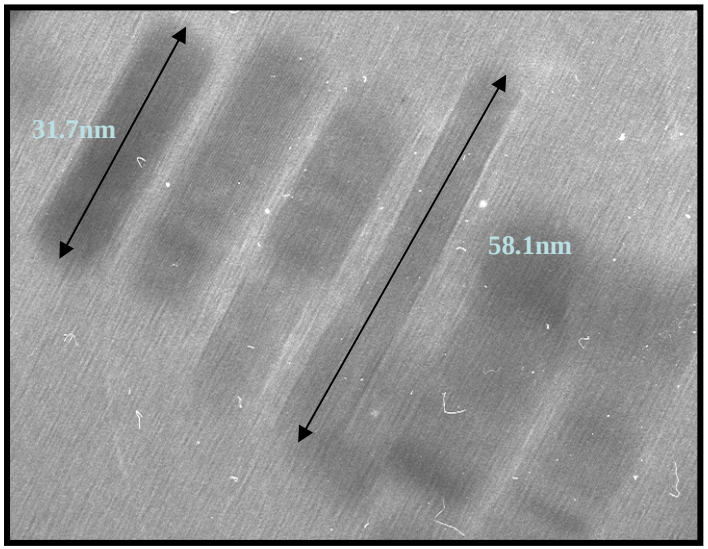


PbS rods, bipods and tripods





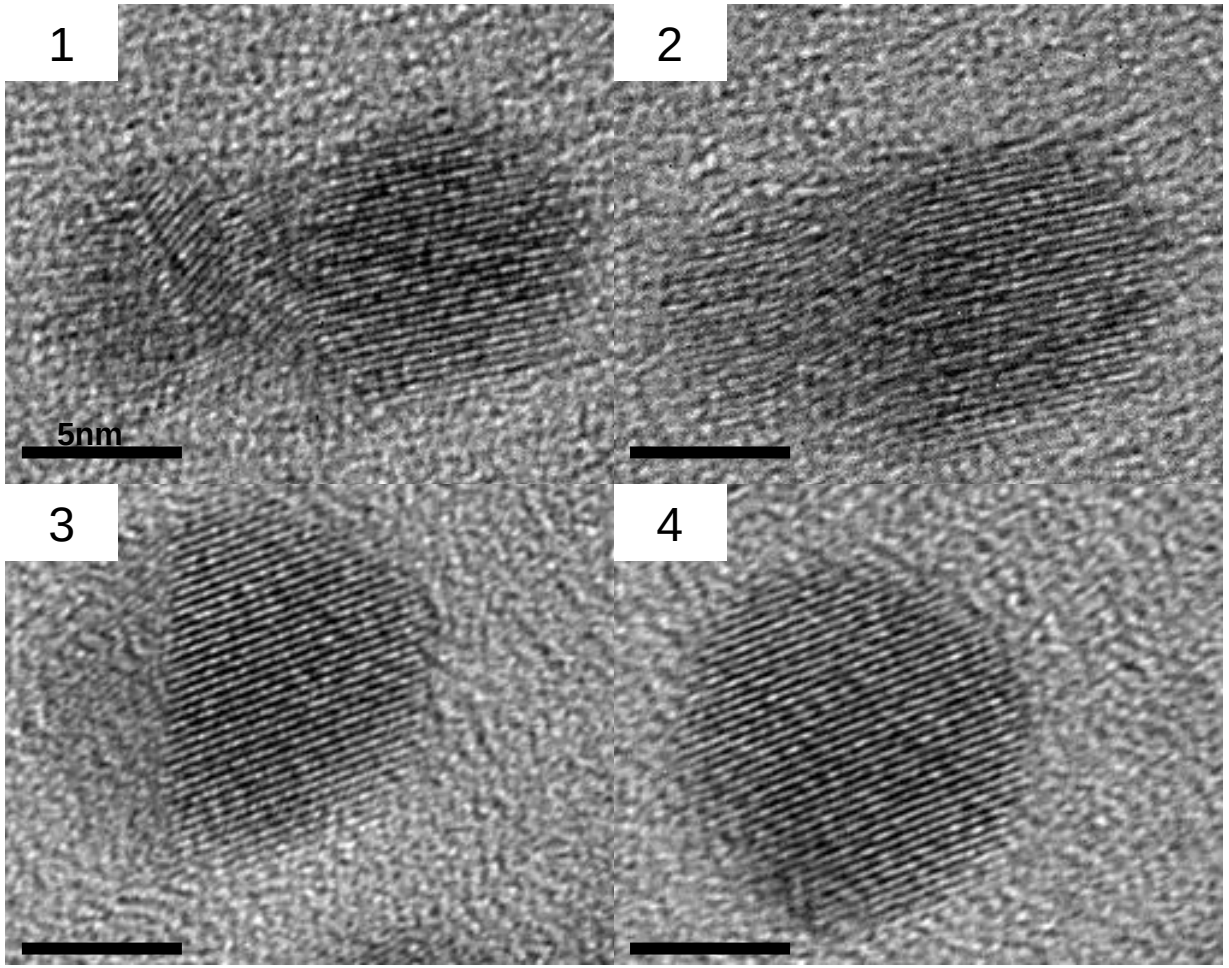


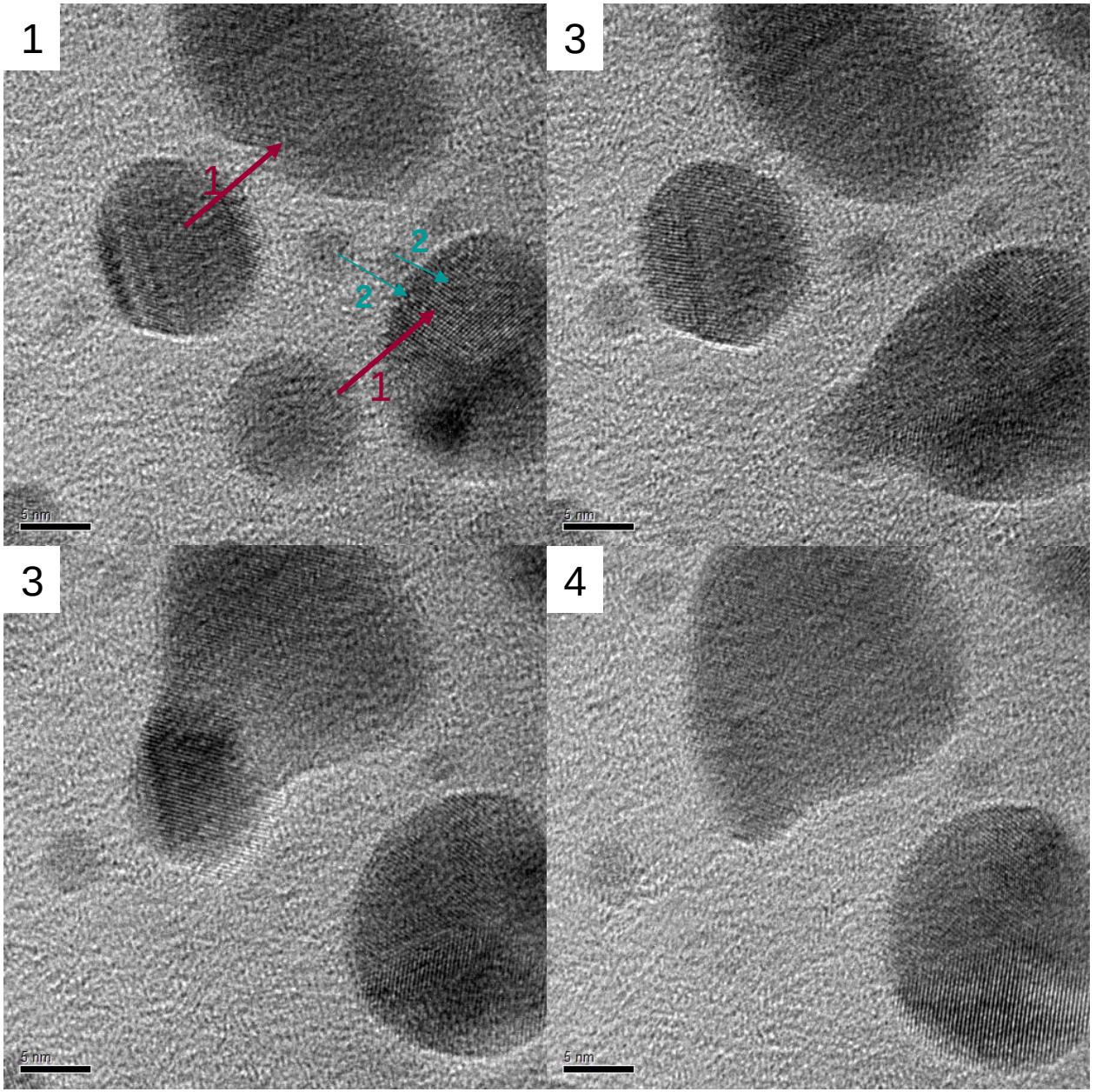


Bernau, O'Brien, Smyth-Boyle,

Chemical Communication 2006 on web

ELECTRON BEAM INDUCED RIPENING PROCESS

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1
2
2
1
5 nm
3
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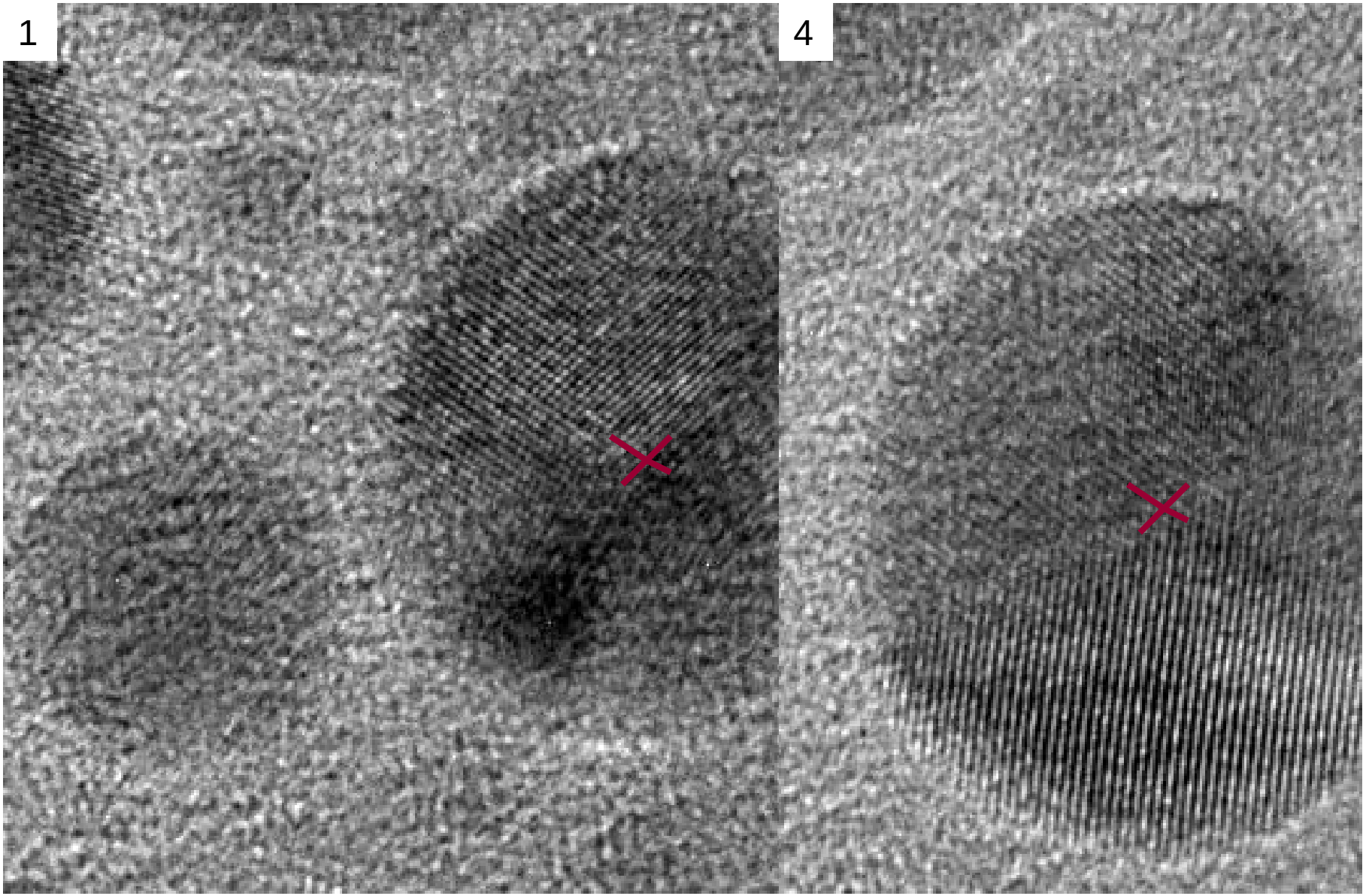
4
5 nm


1
4

AS for SA.ppt

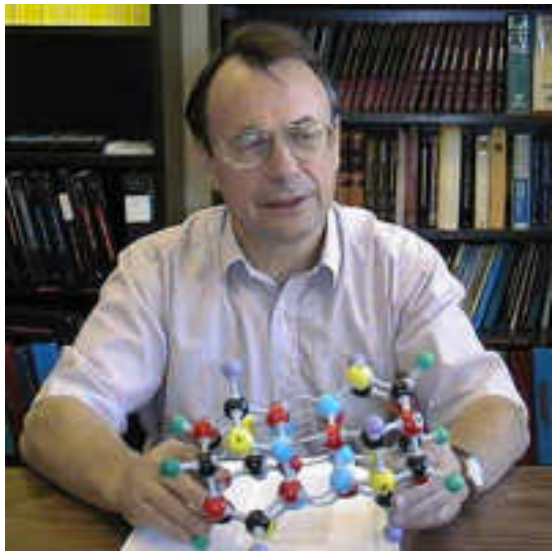
MANCHESTER
1824

The University of Manchester

Combining the strengths of UMIST and
The Victoria University of Manchester

Thanks

- EPSRC
- RCUK
- University of Manchester
- Royal Society



- Mohammed Afzaal
- Chin Ngyuan
- Azad Malik
- Shivram Garj (Boyscast)
- J.P.Thomas
- ‘Bobo’ Wang
- LeiZhou