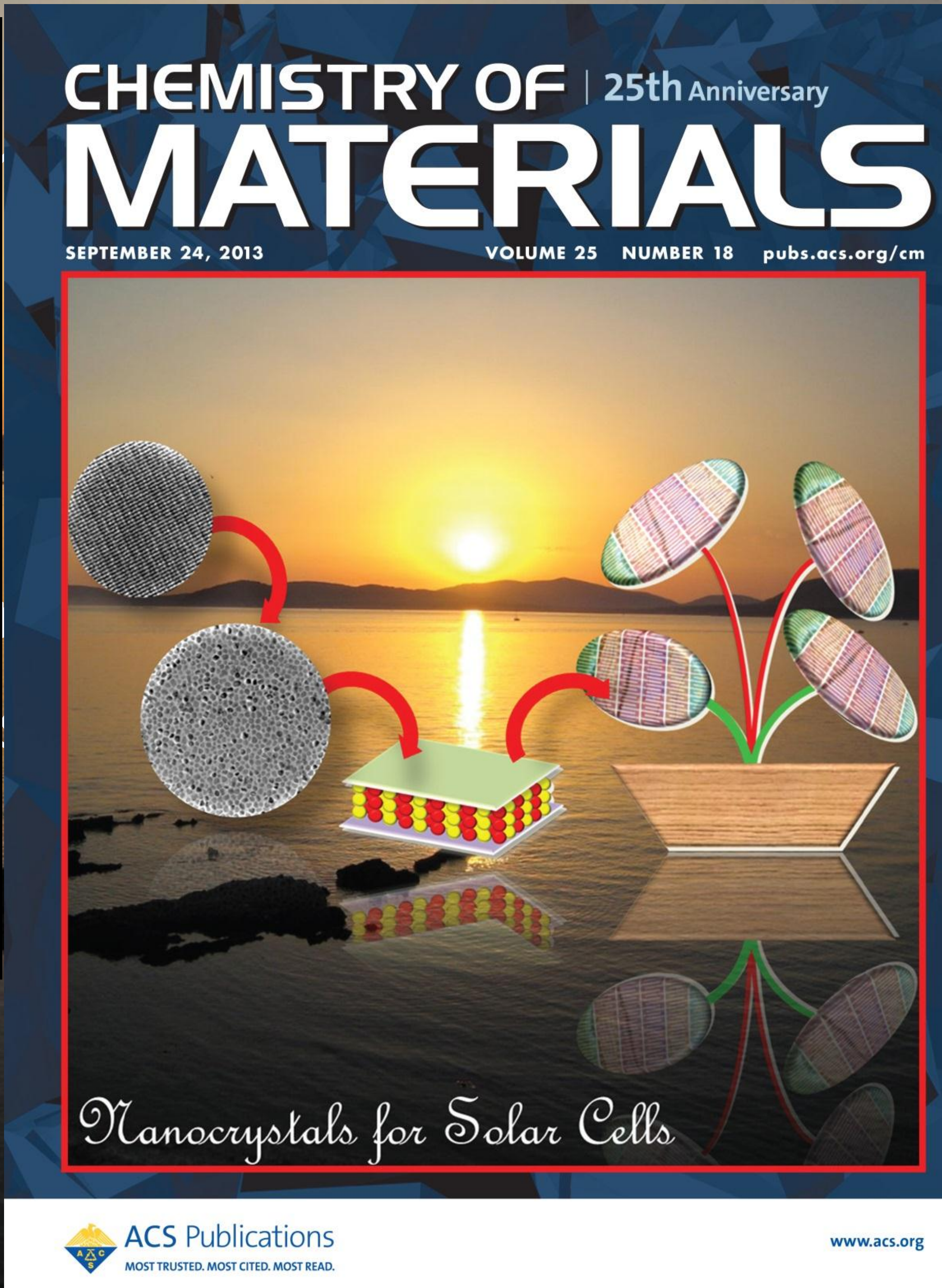
Routes to Nanostructured Inorganic Materials with Potential for Solar Energy Applications

Karthik Ramasamy ‡, Mohammad Azad Malik †, Neerish Revaprasadu §, and Paul O'Brien

Chem. Mater., 2013, 25 (18), pp 3551–3569
DOI: 10.1021/cm401366q

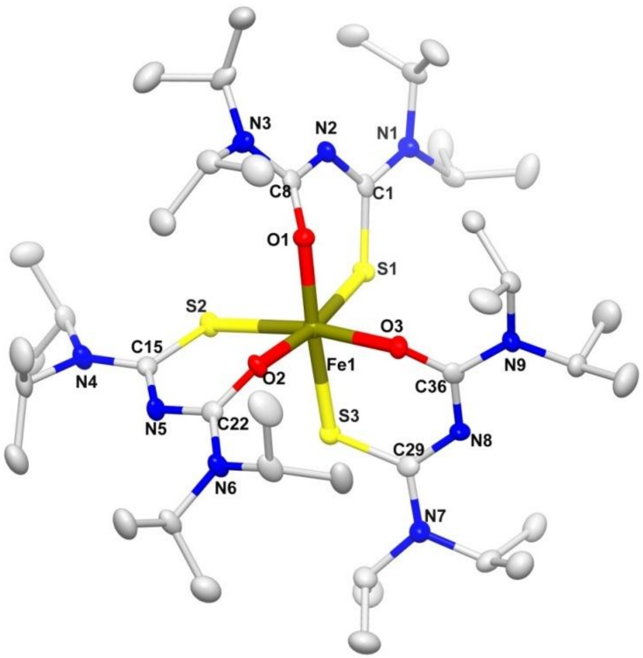


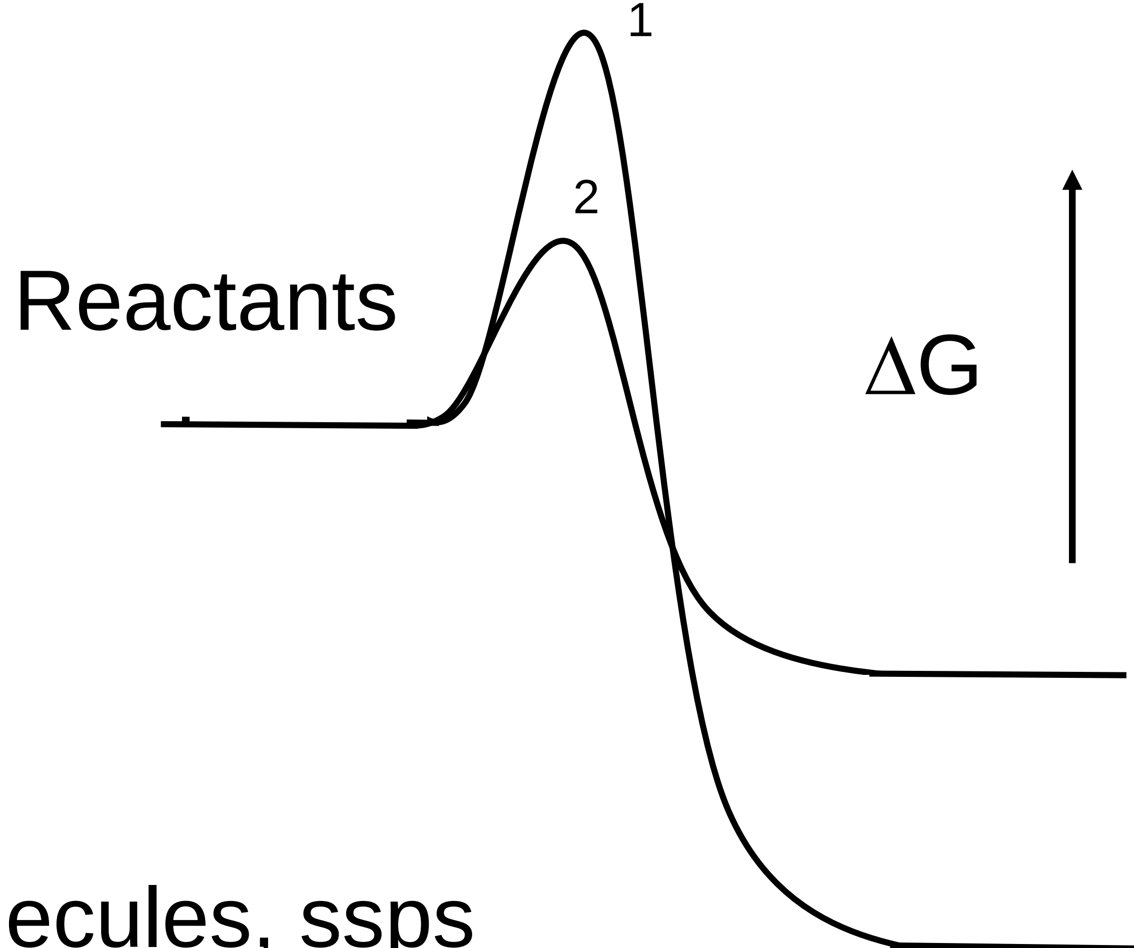
FAPESP WEEK LONDON
BRAZIL - EUROPE SCIENTIFIC COOPERATION

Why use chemistry at all ?

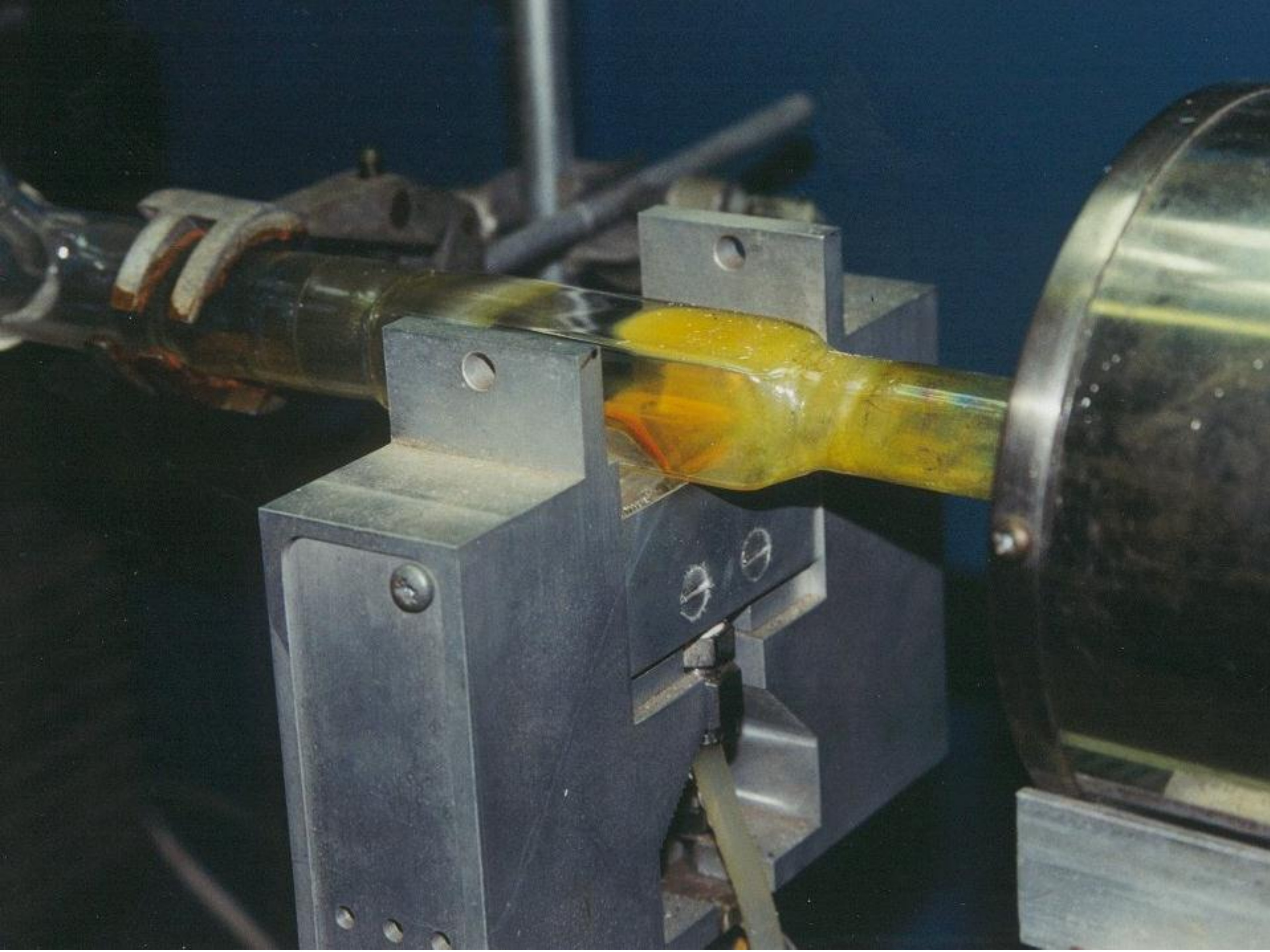
- CVD precursors and control
- Nanoco
- Nanoparticles from solution-crystal formation

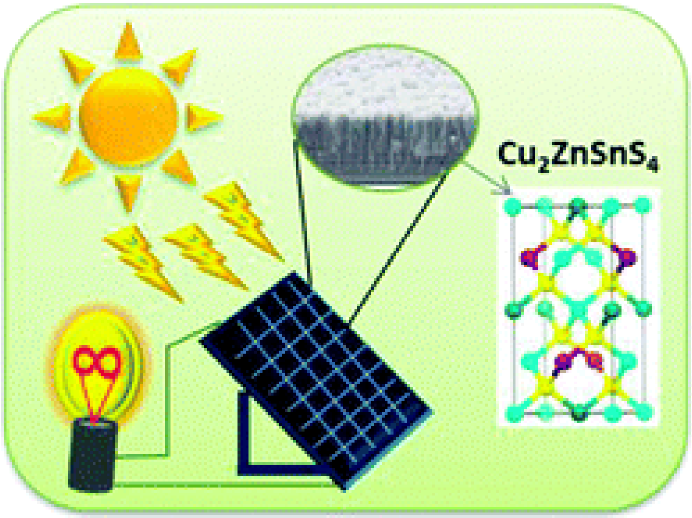
We Can Think of Routes

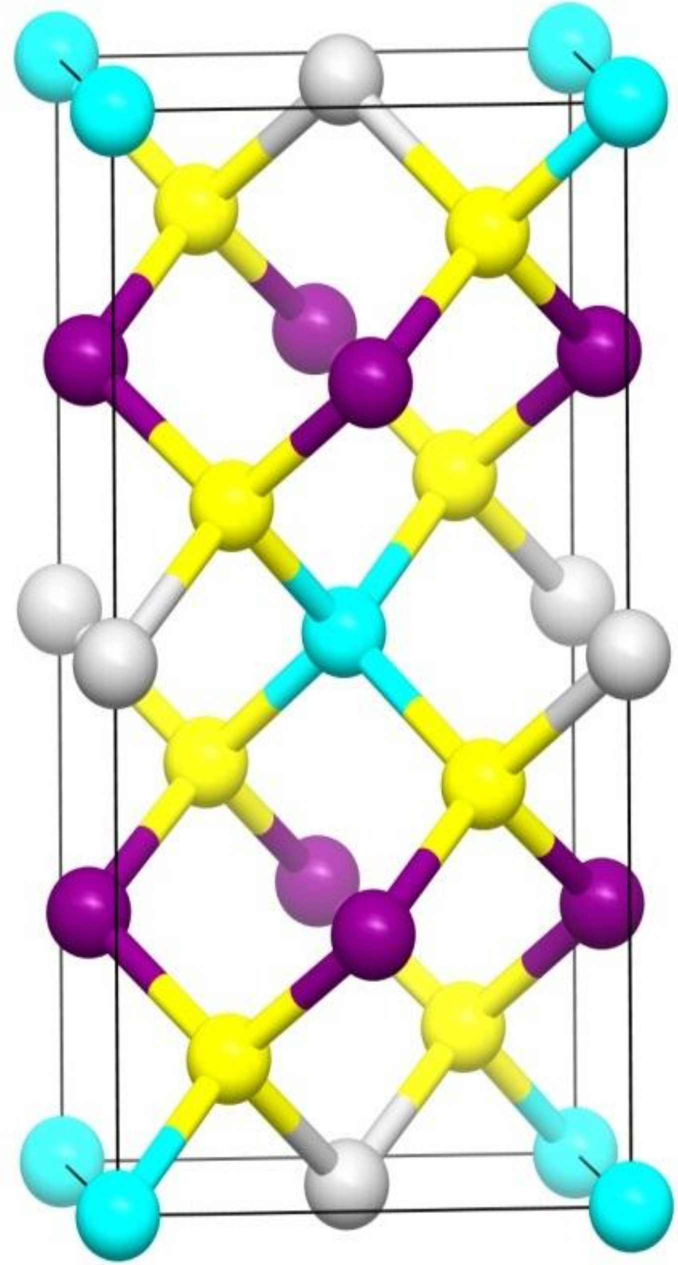




Reactions molecules, ssps
or ions e.g. $Cd^{2+} + S^{2-}$







Routes to copper zinc tin sulfide Cu_2ZnSnS_4 a potential material for solar cells

Karthik Ramasamy,[a] Mohammad A. Malik[a] and Paul O'Brien*[a]

Chem. Commun., 2012,**48**, 5703-5714

The chemical vapor deposition of Cu_2ZnSnS_4 thin films

Karthik Ramasamy,[a] Mohammad A. Malik[a] and Paul O'Brien*[a]

Chem. Sci., 2011,**2**, 1170-1172

News & Analysis

Kesterite solar cell claims 9.6 efficiency

R. Colin Johnson for [EE Times Asia]()

2/16/2010 11:05 AM EST

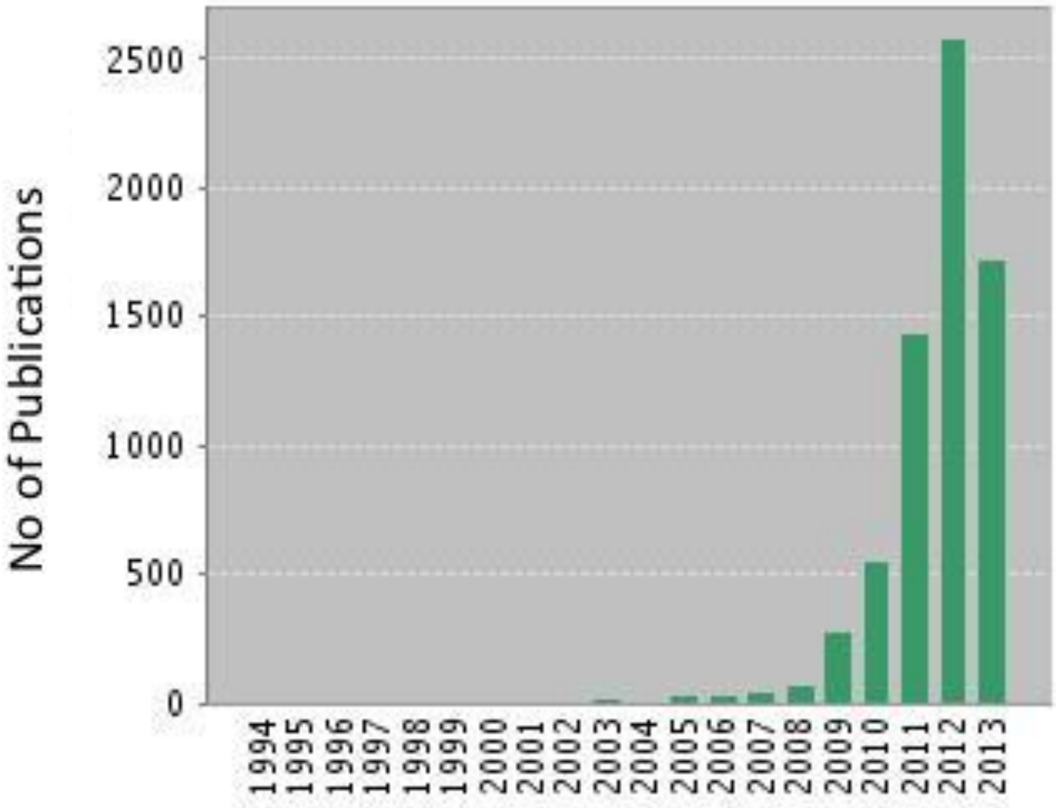
Thin-film solar cells hold the promise of low-cost, renewable energy source that could make fossil fuels obsolete, but thus far the cells' reliance on rare elements and expensive vacuum deposition manufacturing has impeded their progress. IBM Research has proposed solutions to both stumbling blocks by demonstrating a photovoltaic cell that uses common, abundant elements and is produced using an inexpensive nanoparticle- and spin-coat-based "printing" technique.

With 9.6 percent efficiency, the so-called kesterite solar cell beats the previous efficiency record of 6.8 percent for similar structures, bringing kesterite closer to the efficiency of established solar cell formulations, IBM said.

More information:

-- High-Efficiency Solar Cell with Earth-Abundant Liquid-Processed Absorber, *Advanced Materials,* DOI:10.1002/adma.200904155

-- IBM's Smarter Planet Blog



1. H. Katagiri, *Thin Solid Films,*2005, **515**, 480; K. Jimbo, R. Kinura, T. Kamimura, S. Yamada, W. S. Maw, H. Araki, K. Oishi, H. Katagiri, *Thin Solid Films*, 2007, 5997.
2. A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kotschau, H. W. Schock, R. Schurr, A. Holzing, A. Jost, R. Hock, T. Voß, J. Schulze, A. Kirbs, *Thin solid Films*, 2009, **517**, 2511.

Kesterite Cu_2ZnSnS_4

Simple Molecules To Compound Semiconductor

$[Cu(S_2CNEt_2)_2]$

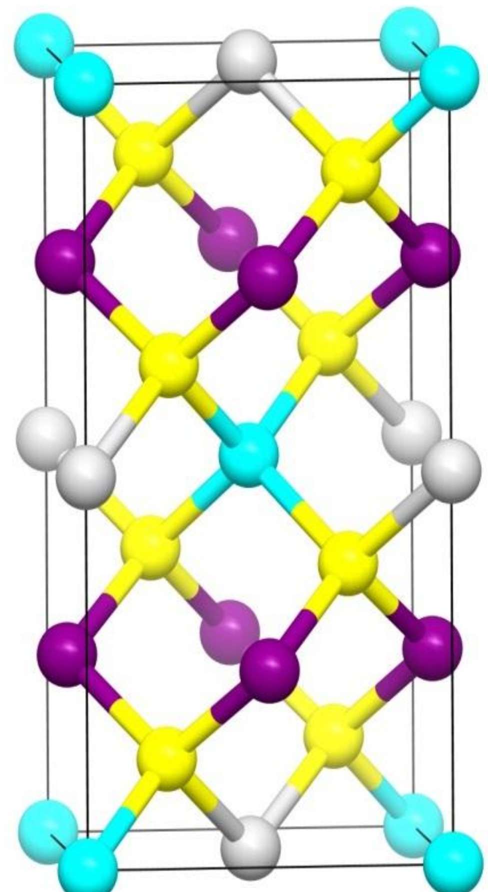
+

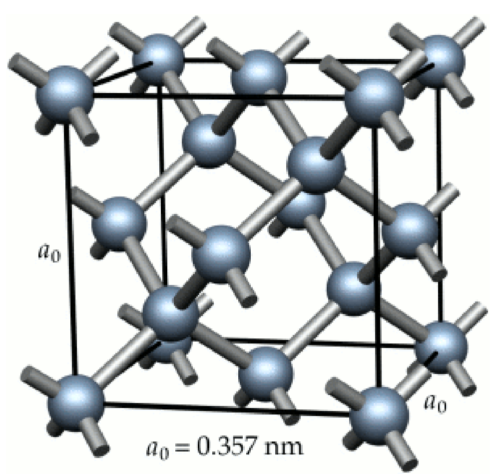
$[Zn(S_2CNEt_2)_2]$

+

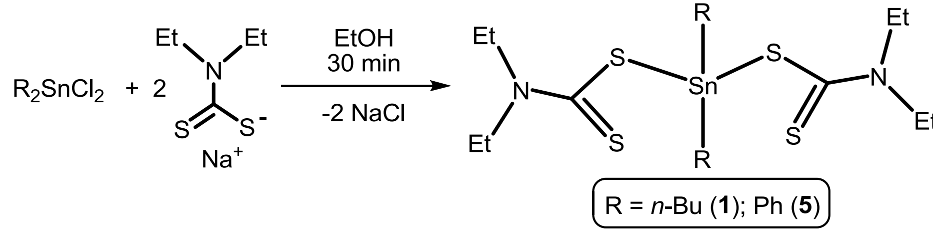
$[Sn(Bu)_2(S_2CNEt_2)_2]$

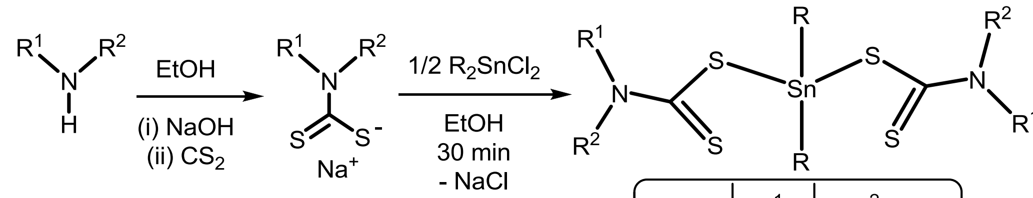
$\xrightarrow{\textbf{CVD}}$



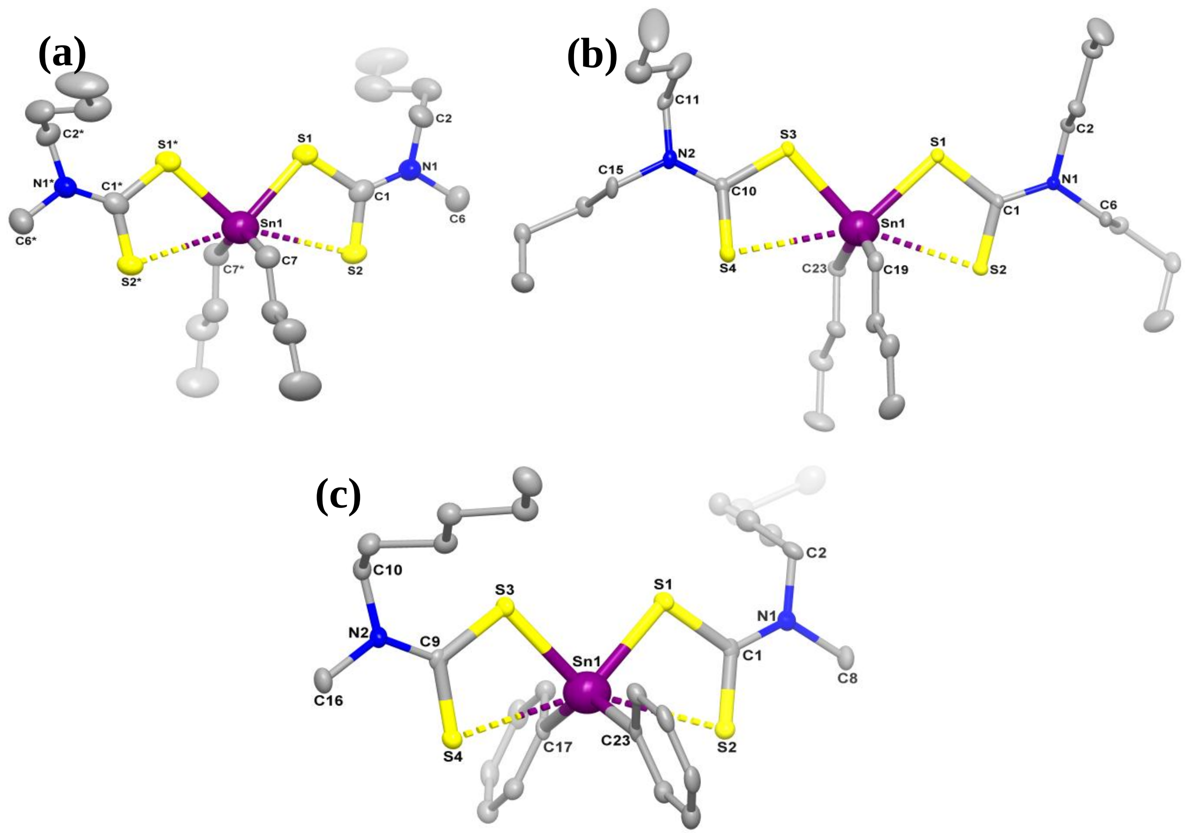


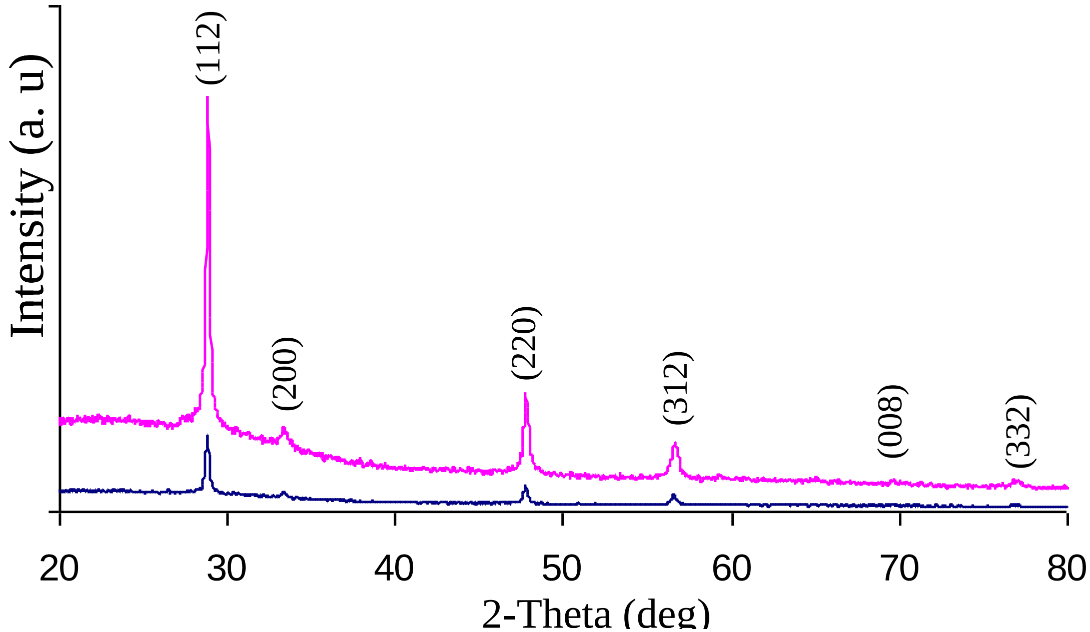
Making Precursors



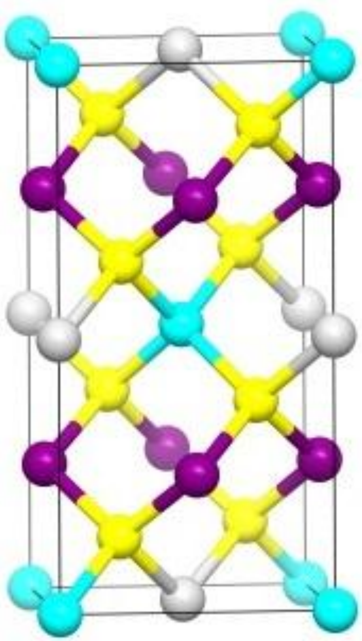


R	R^1	R^2
n-Bu	Me	*n*-Bu (**2**)
n-Bu	*n*-Bu	*n*-Bu (**3**)
n-Bu	Me	*n*-Hex (**4**)
Ph	Me	*n*-Bu (**6**)
Ph	*n*-Bu	*n*-Bu (**7**)
Ph	Me	*n*-Hex (**8**)

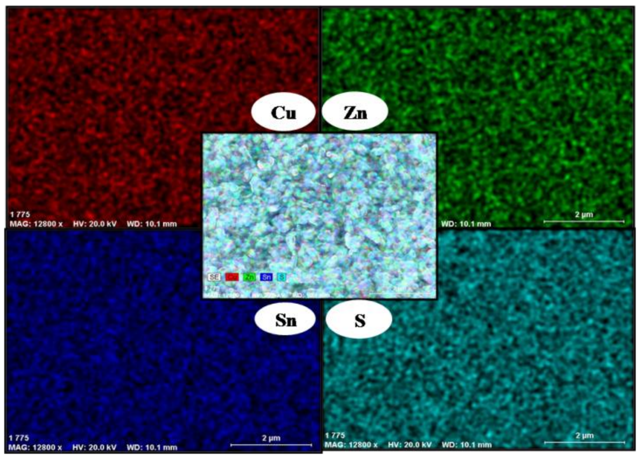




PXRD pattern of CZTS thin films deposited at a) 360 ºC and b) 400 º C.
Inset conventional unit cell structure of CZTS



[The chemical vapor deposition of Cu_2ZnSnS_4 thin films, K. Ramasamy, M. A. Malik, P. O'Brien, Chem. Sci. 2011; 2; 1170-1172.]



EDX elemental mapping graph of films deposited at 360 ºC.

Who is Nanoco?

- **Nanotechnology Spun-out from University of Manchester established in 2002**
- **Manufacturing company, producing fluorescent semiconductor nanoparticles "quantum dot“ and quantum dot products**
- **Develop and own key technology and intellectual property for the production of Quantum Dots**
- **Manufacture Quantum Dots which is a “platform technology” with many applications in different industry sectors**
- **Currently supply emerging research and commercial markets with prefabricated quantum dots**

Structure of the Talk

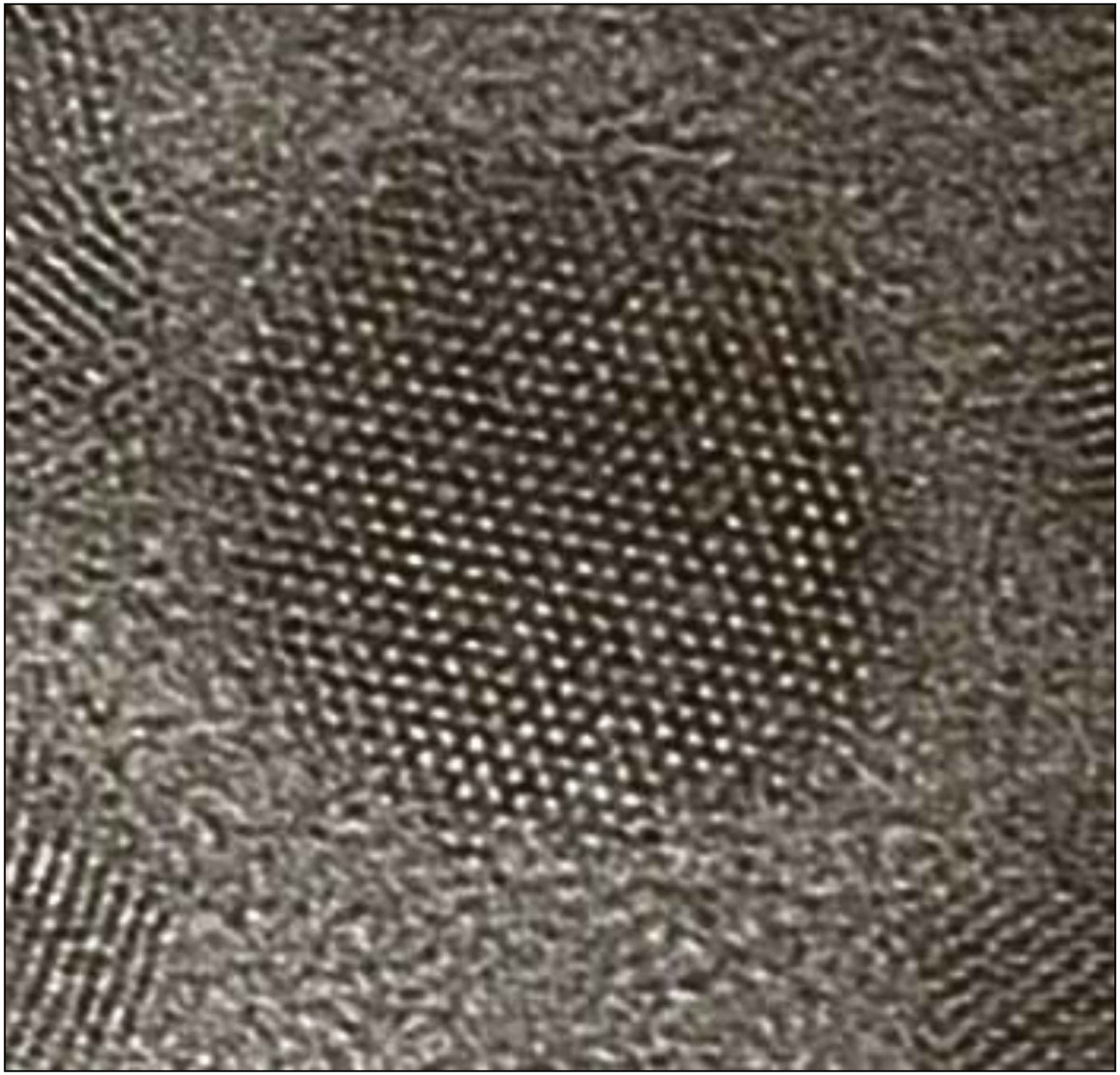
- **The technology**
- **Why be involved in a start up?**
- **How it happened- early days- IP**
- **First funding and rapid growth**
- **Listing and after success and scars**
- **POB as a founder perspective**
- **Other paradigms and other countries**
- **Further reading**

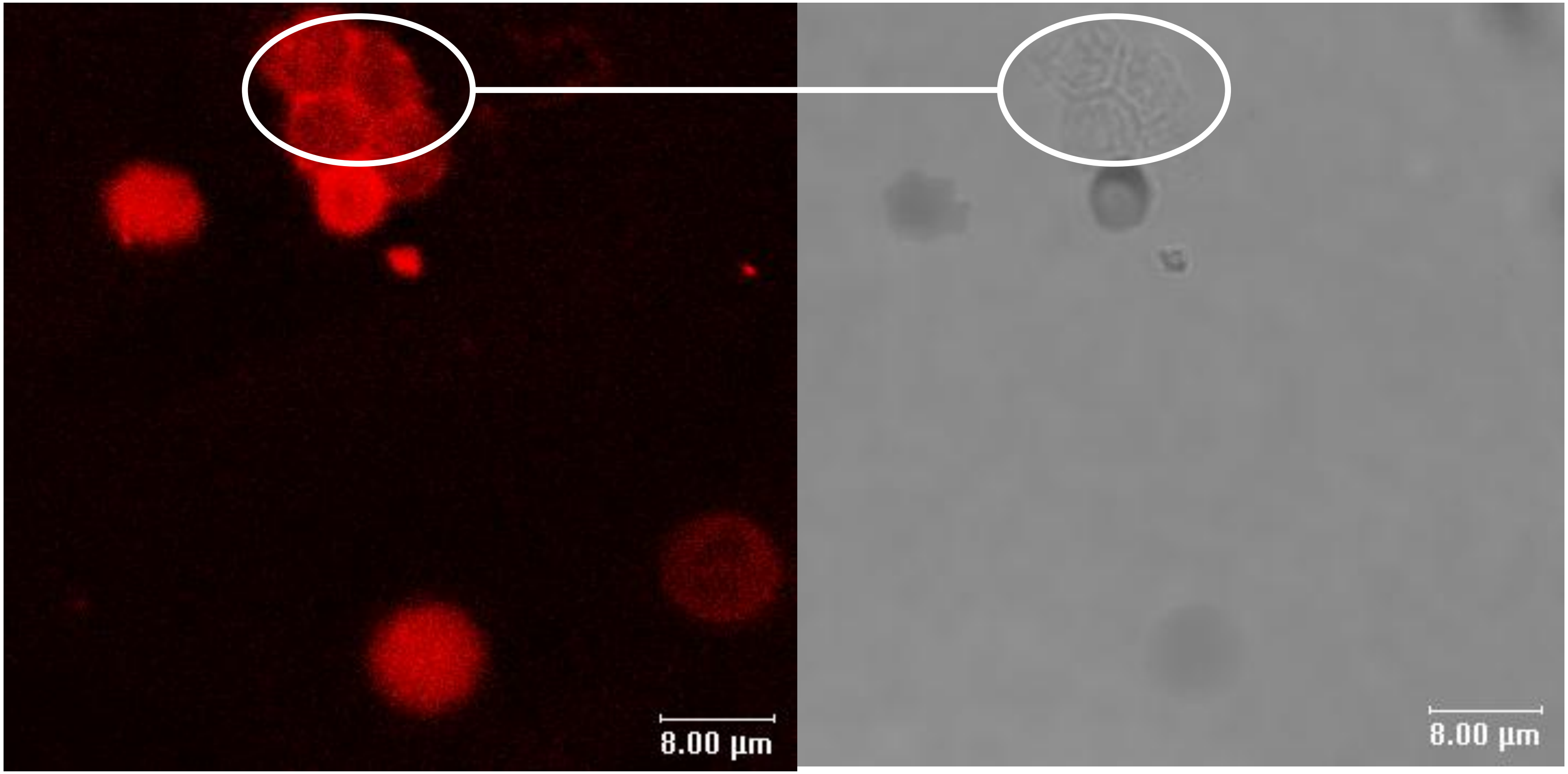
What are Quantum Dots?

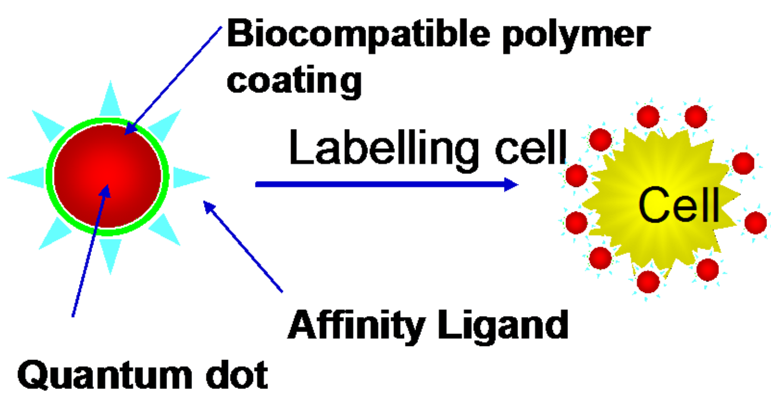
- Semiconductor material 100,000 x smaller than the width of a human hair
- Size gives unique electronic and optical properties
- Platform technology with many applications across different industry sectors

Why use them?

- Replacement for luminescent dyes and inorganic materials
- Better optical and electronic efficiencies
  – More stable
  – More versatile
- True platform technology which can be utilized in a range of applications across different industries

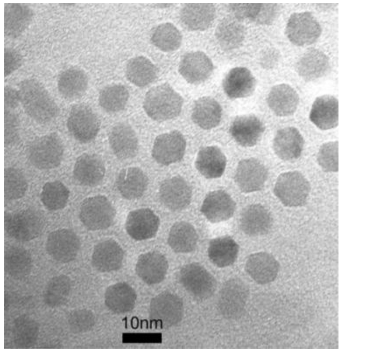






http://www.invitrogen.com/site/us/en/home/Products-and-Services/Applications/Cell-Analysis/qdots-microspheres-nanospheres.html

Nanoco Solves a “Scale up” Problem



The Problem

The existing quantum dot ‘manufacturers’ processes are

- Complex
  - Hazardous and used banned substances
- Costly
- Low manufacturing yield

Without stable, cost effective supply of larger quantities of quality QD, developers are unable to bring there applications to market

The Solution

Nanoco’s patented technology can

- Using a ‘simple’ and controlled process
- At a low cost
- Now regularly produce r+d batches of 100g- 1 Kg pilot 2011

Nanoco also has world leading patent technology to unlock the market

http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=16376883

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Why Do This Activity?

Three reasons

- **To enjoy it**
- **To make the world a better place**
- **To make money**

Why Do This Activity?

Three reasons

To enjoy it----Academic?

To make the world a better place--Academic ?

To MAKE MONEY ----A VC√ An Academic?

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Time Line How it Happened

1996 Patent granted 2002

Process for preparing a Nanocrystalline Material, P. O'Brien and T. Trindade, United States Patent No: 6,379,635 B2.

2002 Nanoco Ltd formed
2002 Runner up DTI Business Plan competition
2004 SMART Award
2005 First funding £600 k (ME appointed)
2006 Serious funding > £2 M (10 or 12 PDRAs!)
2007 Move to Incubator
2009 April reverse onto AIM
2010 £2 M milestone achieved
2011 Kilogram production

Two CEOs

Nob Tamegawa!

Other Investments..

Where did it come from Nanoco?

QM then Imperial College Decision to Patent

1996 decision to patent
Complex-methods
- Hazardous and used banned substances
- Costly
- Low manufacturing yield
  - No-one can produce a 1g batch

Without stable, cost effective supply of larger quantities of quality QD, developers are unable to bring there applications to market

The Solution

What became Nanoco's patented technology which can
- Using a 'simple' and controlled process
- At a low cost
- Now regularly produce r+d batches of 100g

Nanoco now has world leading patent technology to unlock the market

US 20010005495A1

(19) **United States**

(12) **Patent Application Publication**

O'BRIEN et al.

(10) **Pub. No.: US 2001/0005495 A1**

(43) **Pub. Date: Jun. 28, 2001**

(54) **PROCESS FOR PREPARING A NANOCRYSTALLINE MATERIAL**

(75) Inventors: **PAUL O'BRIEN**, ESSEX (GB); **TITO TRINDADE**, ICHAVO (PT)

Correspondence Address:
THOMAS J KOWALSKI
FROMMER LAWRENCE & HAUG
745 FIFTH AVENUE
NEW YORK, NY 10151

(73) Assignee: **Paul O'Brien**

(*) Notice: This is a publication of a continued prosecution application (CPA) filed under 37 CFR 1.53(d).

(21) Appl. No.: **09/043,258**

(22) PCT Filed: **Aug. 9, 1996**

(86) PCT No.: **PCT/GB96/01942**

(30) **Foreign Application Priority Data**

Sep. 15, 1995 (GB) 9518910.6

Publication Classification

(51) **Int. Cl.**[7] **C01G 21/00**; C01G 11/00; C01G 15/00; C01G 9/00; C01F 7/00; C01G 13/00

(52) **U.S. Cl.** **423/87**; 423/92; 423/101; 423/122; 423/509; 423/566.1

(57) **ABSTRACT**

A process for preparing a nanocrystalline material comprising at least a first ion and at least a second ion different from the first ion, and wherein at least the first ion is a metal ion, is described. The process comprises contacting a metal complex comprising the first ion and the second ion with a dispersing medium suitable to form the nanocrystalline material and wherein the dispersing medium is at a temperature to allow formation by pyrolysis of the nanocrystalline material when contacted with the metal complex.

http://www.us-patent-search.com/

WIMPS!

"You're ripping us off!", Steve shouted, raising his voice even higher. "I trusted you, and now you're stealing from us!"

But Bill Gates just stood there coolly, looking Steve directly in the eye, before starting to speak in his squeaky voice.

"Well, Steve, I think there's more than one way of looking at it. I think it's more like we both had this rich neighbor named Xerox and I broke into his house to steal the TV set …"

"and found out that you had already stolen it."

Why Patent What to Patent

- What is a patent what does it do

- Why file
  - Licencing/Sale
  - Start up
  - America-PCT-Japan
- How should you decide if to to progress this route?
- RB story- Ownership
- Patent- Copyright-Trademark Composite IPR

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pened

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Other Investments..

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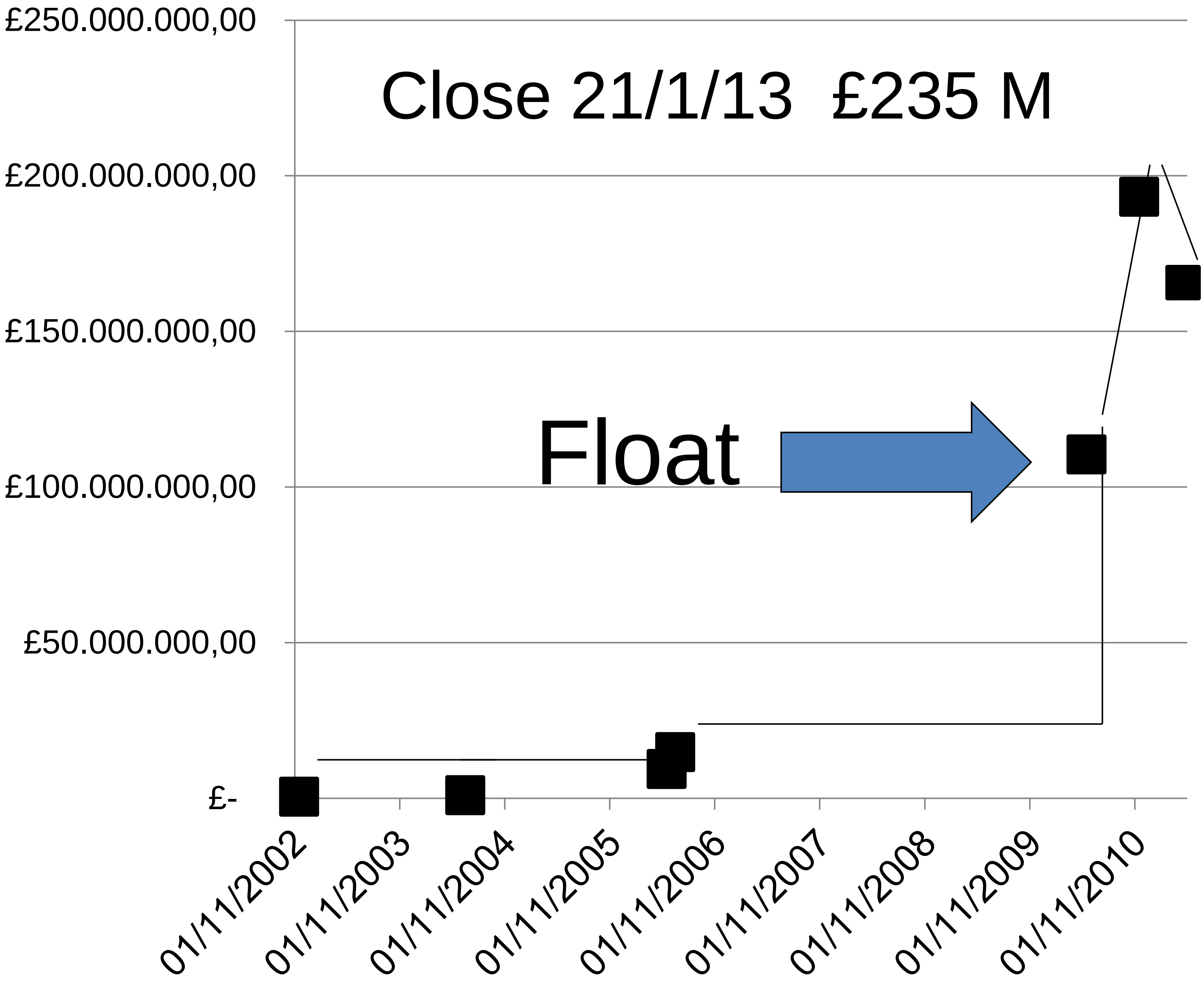
Value of Company



ON the Web

London Stock Exchange

Share Charts for Nanoco (NANO)

Today *ca 1.71*

Todayhttp://www.lse.co.uk/SharePrice.asp?shareprice=NANO

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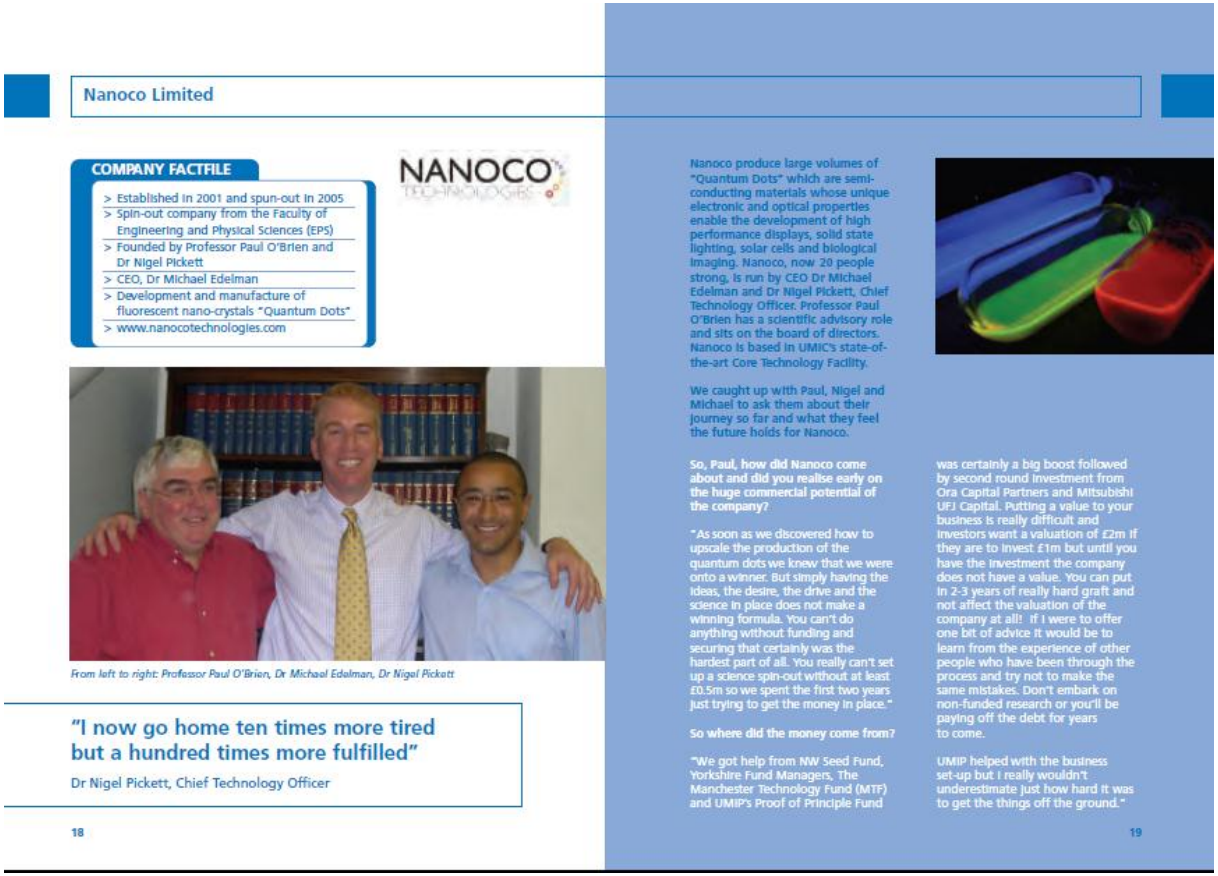

Nanoco Limited

COMPANY FACTFILE

- > Established in 2001 and spun-out in 2005
- > Spin-out company from the Faculty of Engineering and Physical Sciences (EPS)
- > Founded by Professor Paul O'Brien and Dr Nigel Pickett
- > CEO, Dr Michael Edelman
- > Development and manufacture of fluorescent nano-crystals "Quantum Dots"
- > www.nanocotechnologies.com

NANOCO TECHNOLOGIES

From left to right: Professor Paul O'Brien, Dr Michael Edelman, Dr Nigel Pickett

"I now go home ten times more tired but a hundred times more fulfilled"

Dr Nigel Pickett, Chief Technology Officer

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Nanoco produce large volumes of "Quantum Dots" which are semi-conducting materials whose unique electronic and optical properties enable the development of high performance displays, solid state lighting, solar cells and biological imaging. Nanoco, now 20 people strong, is run by CEO Dr Michael Edelman and Dr Nigel Pickett, Chief Technology Officer. Professor Paul O'Brien has a scientific advisory role and sits on the board of directors. Nanoco is based in UMIC's state-of-the-art Core Technology Facility.

We caught up with Paul, Nigel and Michael to ask them about their journey so far and what they feel the future holds for Nanoco.

So, Paul, how did Nanoco come about and did you realise early on the huge commercial potential of the company?

"As soon as we discovered how to upscale the production of the quantum dots we knew that we were onto a winner. But simply having the ideas, the desire, the drive and the science in place does not make a winning formula. You can't do anything without funding and securing that certainly was the hardest part of all. You really can't set up a science spin-out without at least £0.5m so we spent the first two years just trying to get the money in place."

So where did the money come from?

"We got help from NW Seed Fund, Yorkshire Fund Managers, The Manchester Technology Fund (MTF) and UMIP's Proof of Principle Fund was certainly a big boost followed by second round investment from Ora Capital Partners and Mitsubishi UFJ Capital. Putting a value to your business is really difficult and investors want a valuation of £2m if they are to invest £1m but until you have the investment the company does not have a value. You can put in 2-3 years of really hard graft and not affect the valuation of the company at all! If I were to offer one bit of advice it would be to learn from the experience of other people who have been through the process and try not to make the same mistakes. Don't embark on non-funded research or you'll be paying off the debt for years to come.

UMIP helped with the business set-up but I really wouldn't underestimate just how hard it was to get the things off the ground."

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http://www.umip.com/pdfs/Cases_Spinouts.pdf

Forget 3D, here comes the QD!! TV Television screens that can be rolled up and carried in a pocket are to become a reality using technology developed by British scientists. Sunday Telegraph

By [Richard Gray](), SCIENCE CORRESPONDENT 11/12/2011

Sir Graham Fry

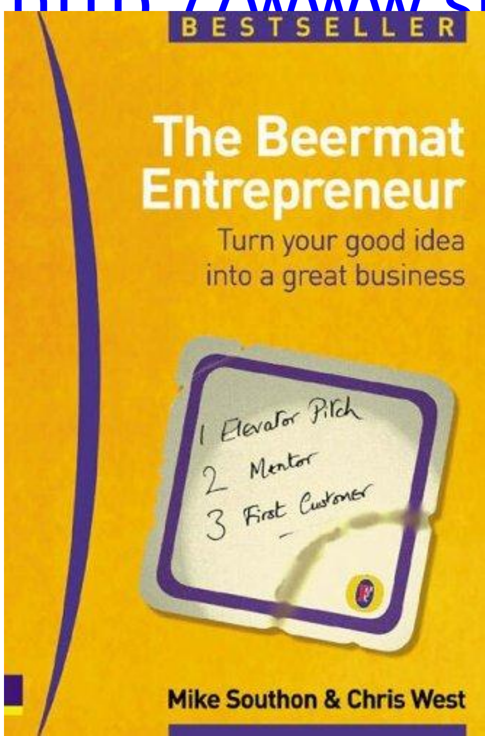
Further Reading

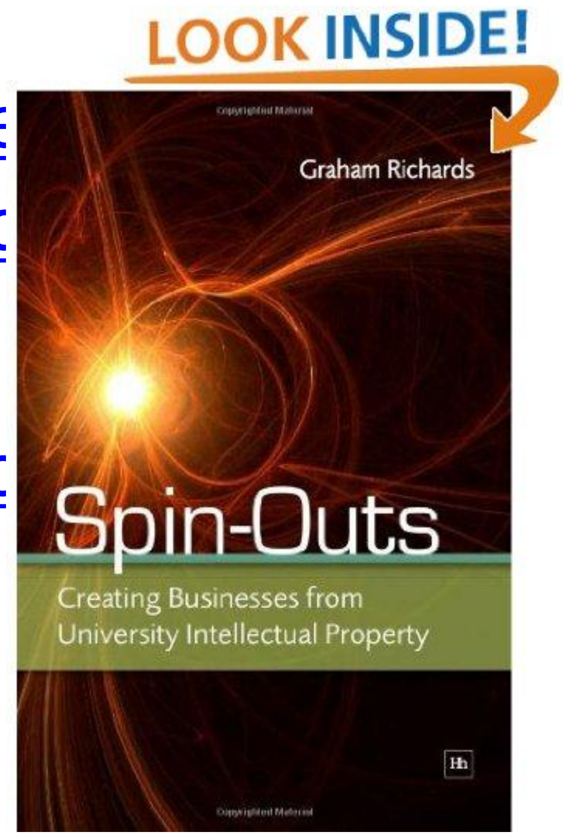
Professor Graham Richards, Oxford Molecular and Inhibox This is Graham Richards's account in his own words…

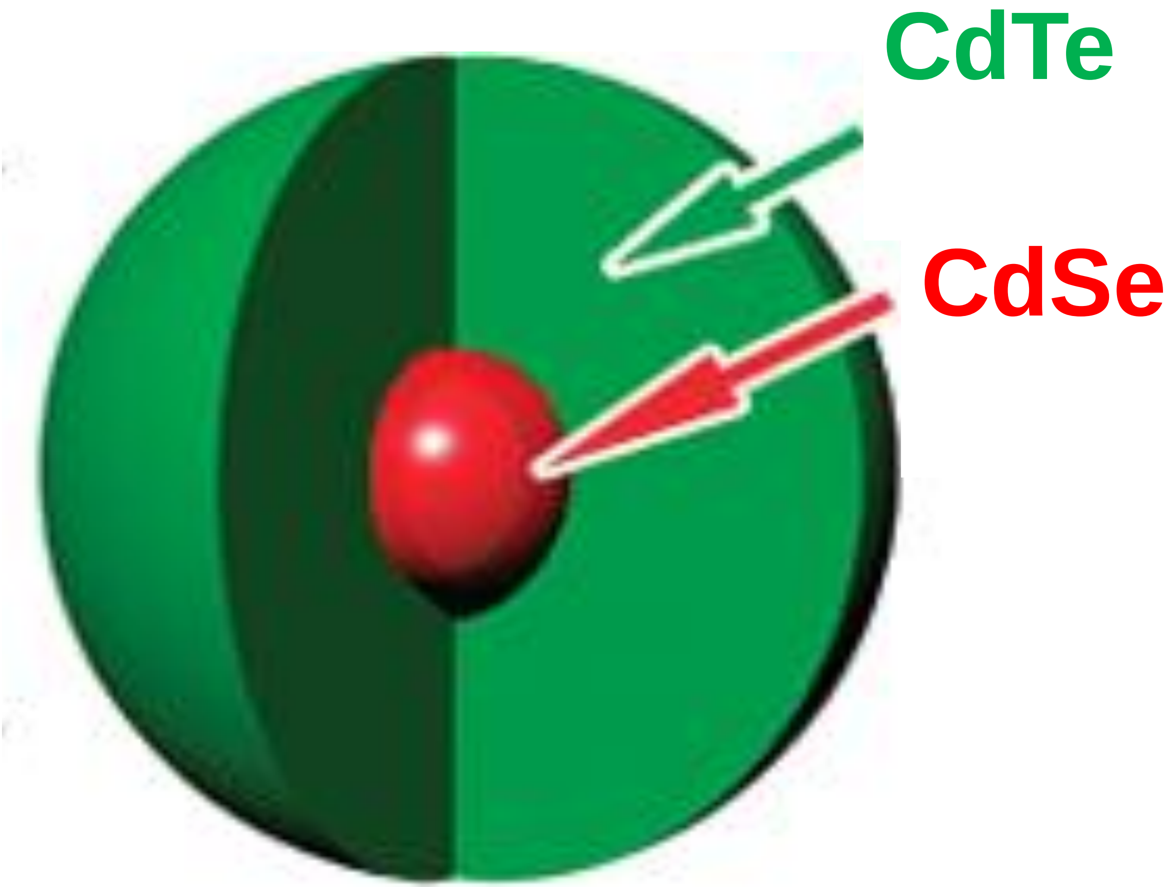
http://www.sbs.ox.ac.uk/centre

ents/Graham_Ric

hibox.com/spin-c







Quantum Dots

Internal Structures

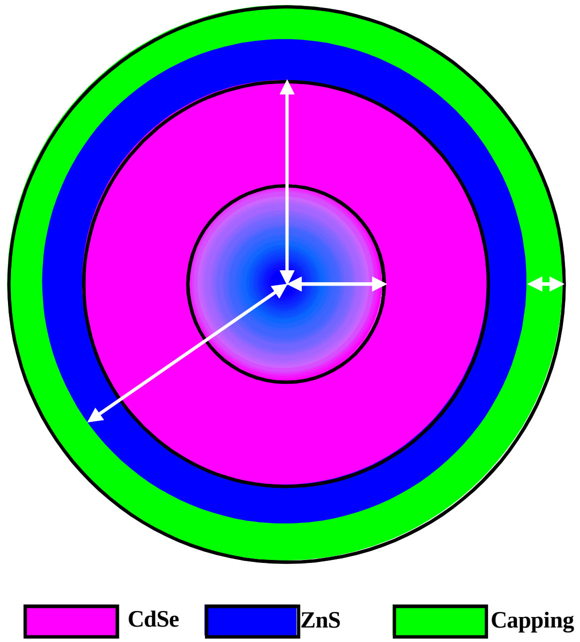


Figure 5a

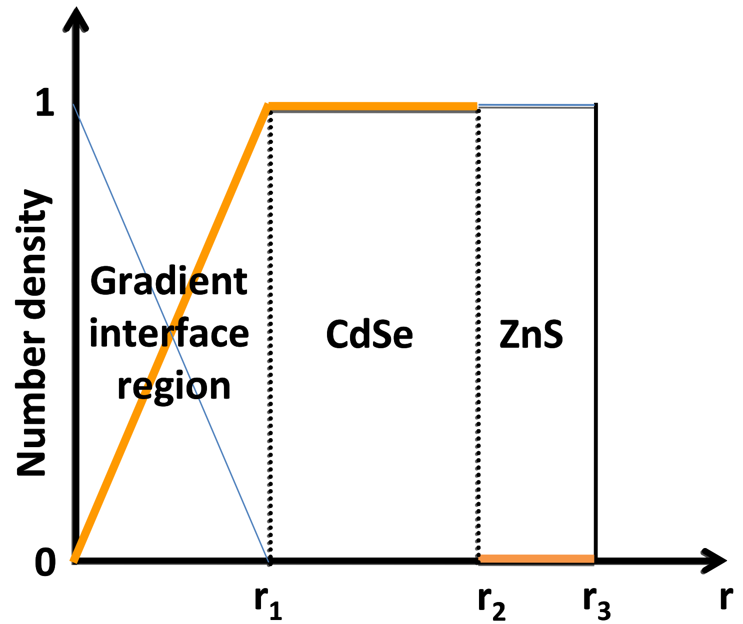
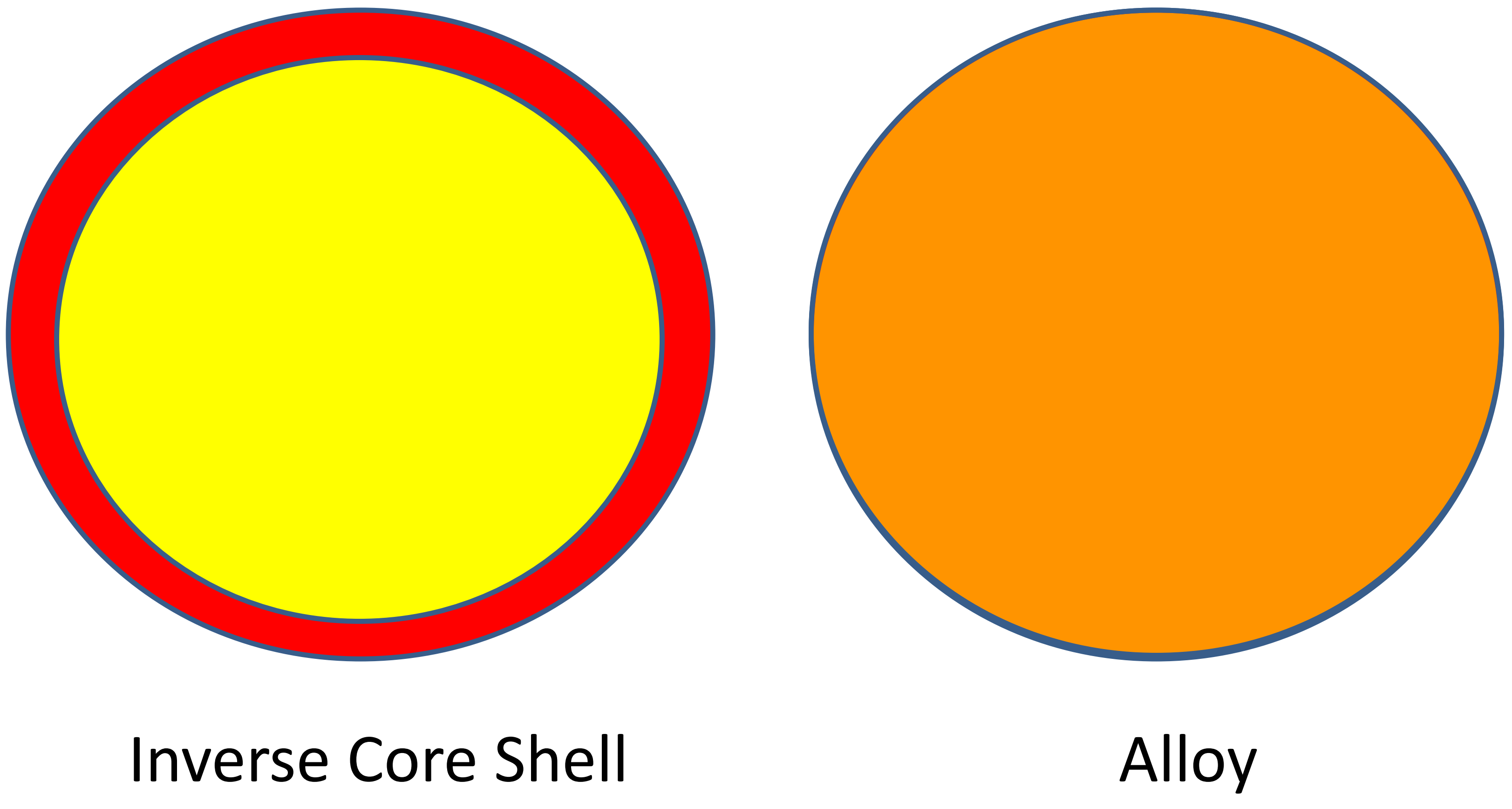
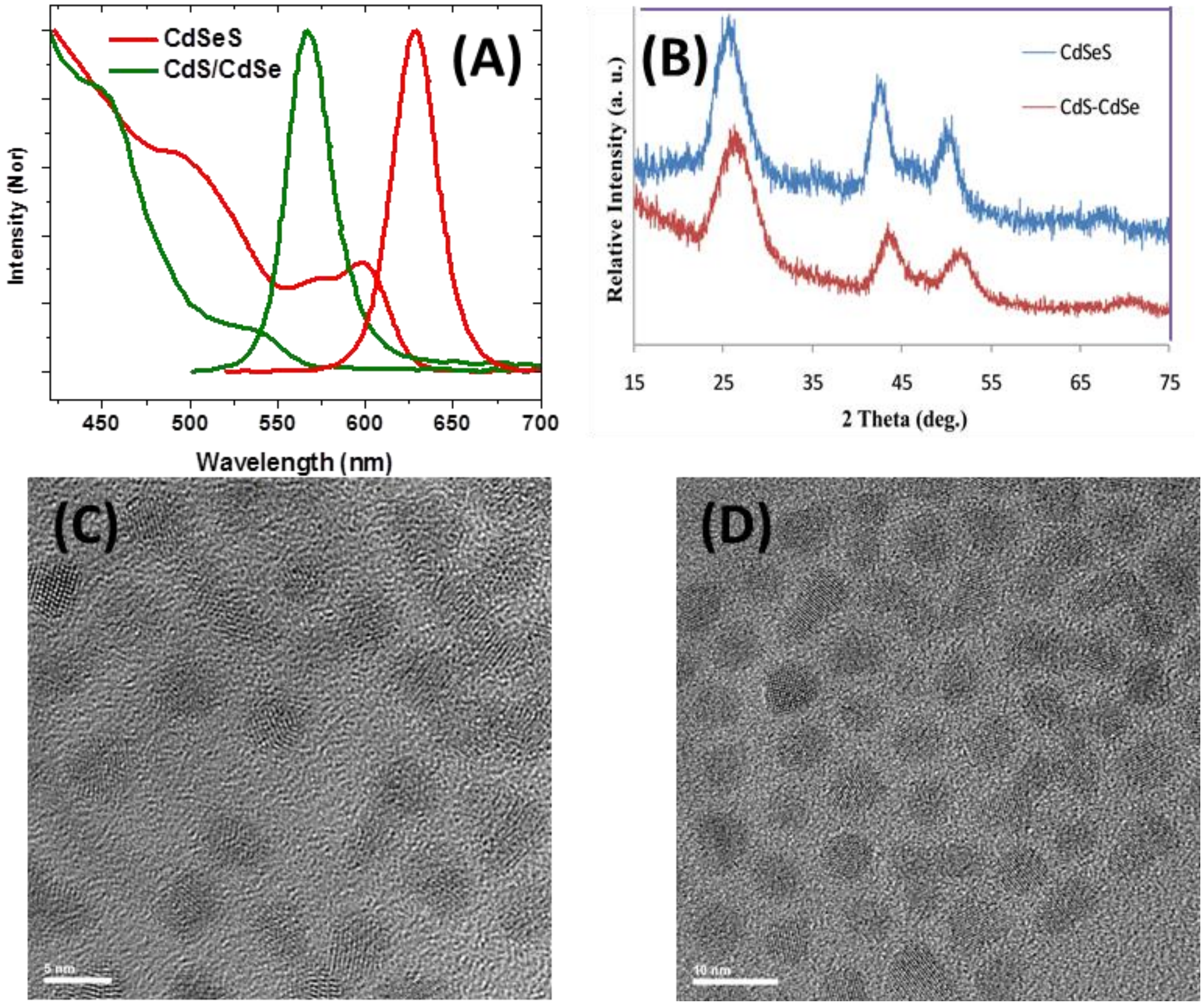


Figure 5b

Schematic model of the heterostructured nanomaterial, which has three main layers. A gradient non homogenous alloy has formed at the core (radius *r1*) followed by a thick shell of the CdSe (from radius *r1* to *r2*) and thinner shell of ZnS (till radius *r3*). (b) Schematic representation of the chemical composition variation for the final model. Investigation of the internal heterostructure of highly luminescent quantum dot-quantum well nanocrystals,
P. K. Santra, R. Viswanatha1, S. M. Daniels, N. L. Pickett, J. M. Smith, P.O'Brien and D. D. Sarma, J.Am.Chem. Soc., 2009, 131, 470-7



Imagined products of Synthesis CdSSe



(A) *UV-Vis and PL data obtained for the inverted core shell (green) and alloyed (red) sample showing the absorption and band edge emmision spectra* (B) *Powder X-Ray diffraction patterns of both the samples showing that the QDs are predominantly in zinc-blend phase* (C) *And* (D) *Transmission Electron Micrographs for the inverted core shell and alloyed sample respectively.*

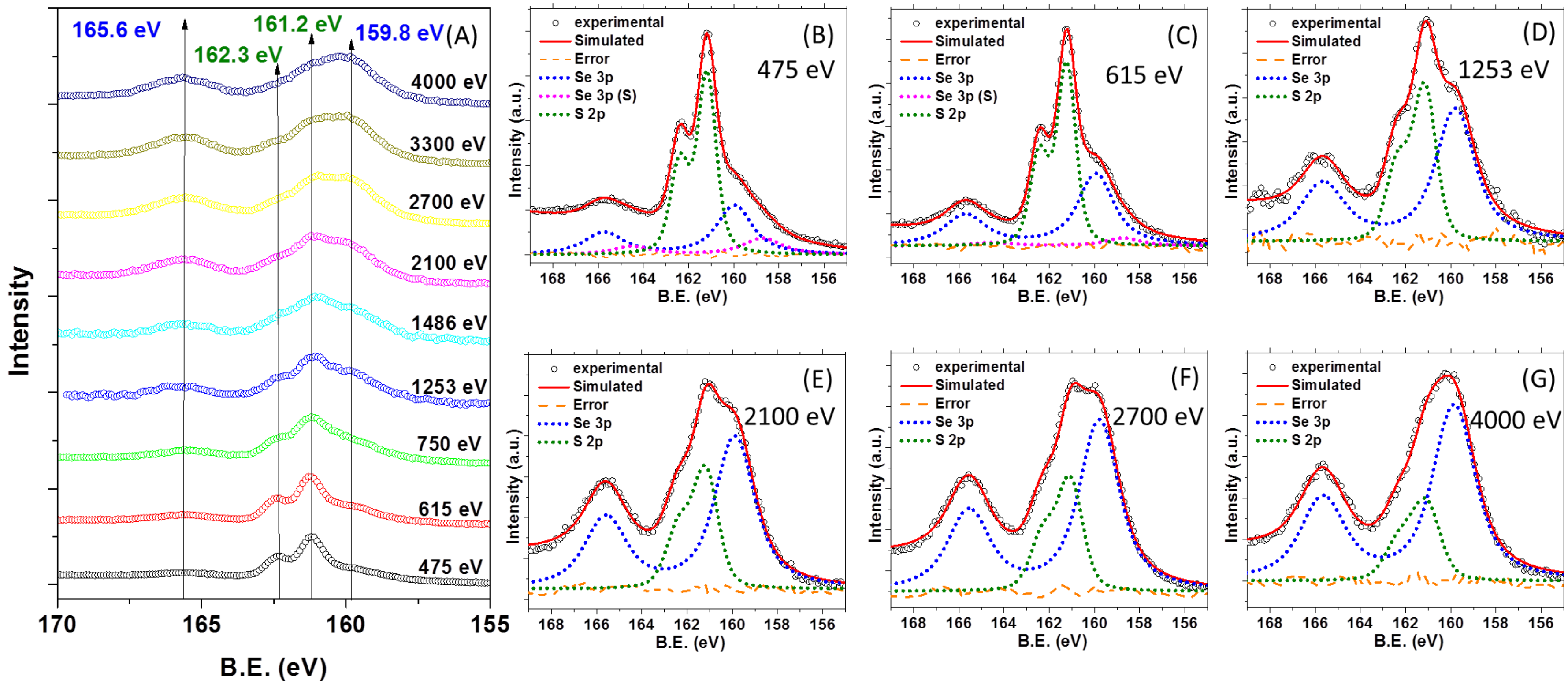
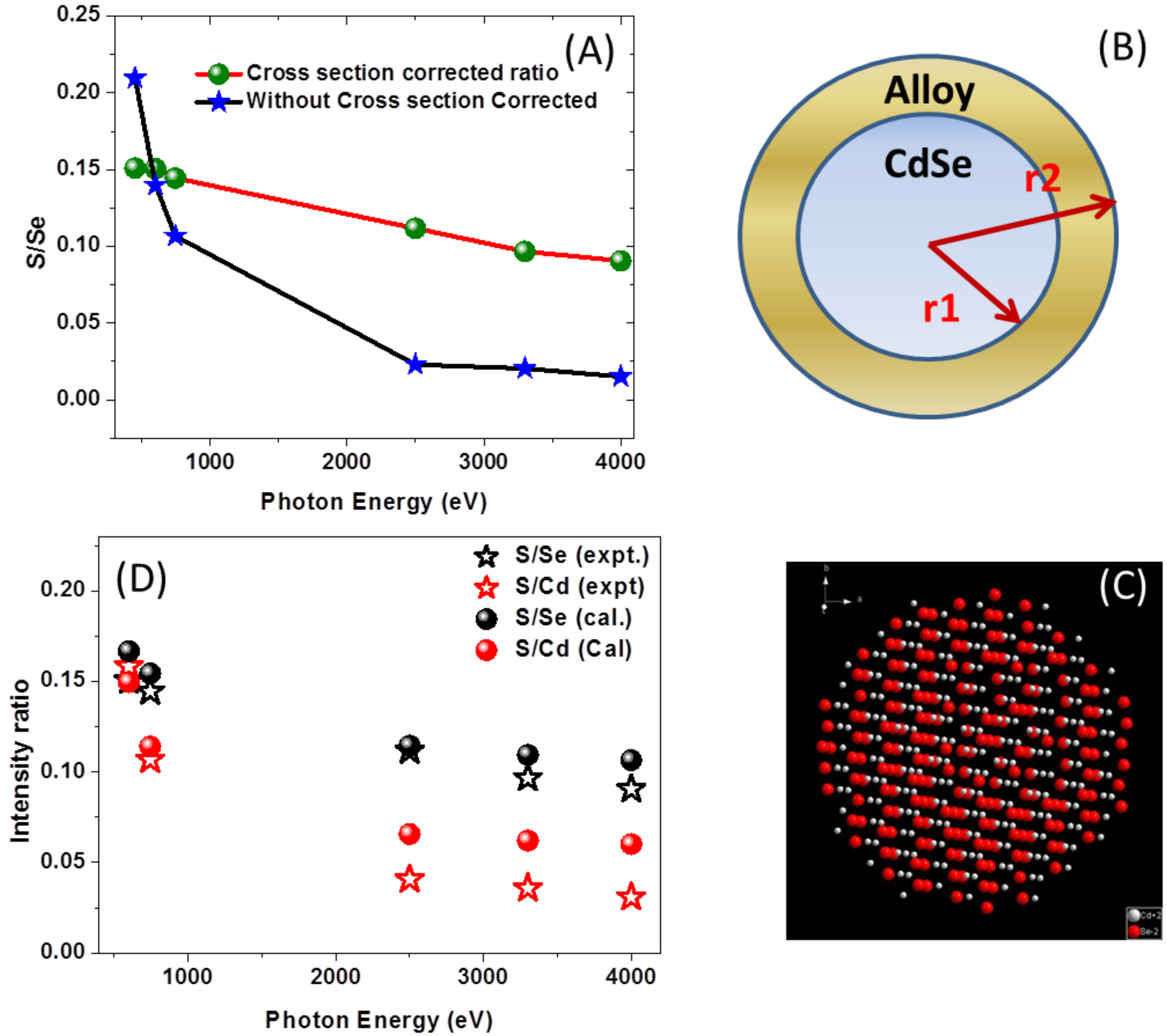
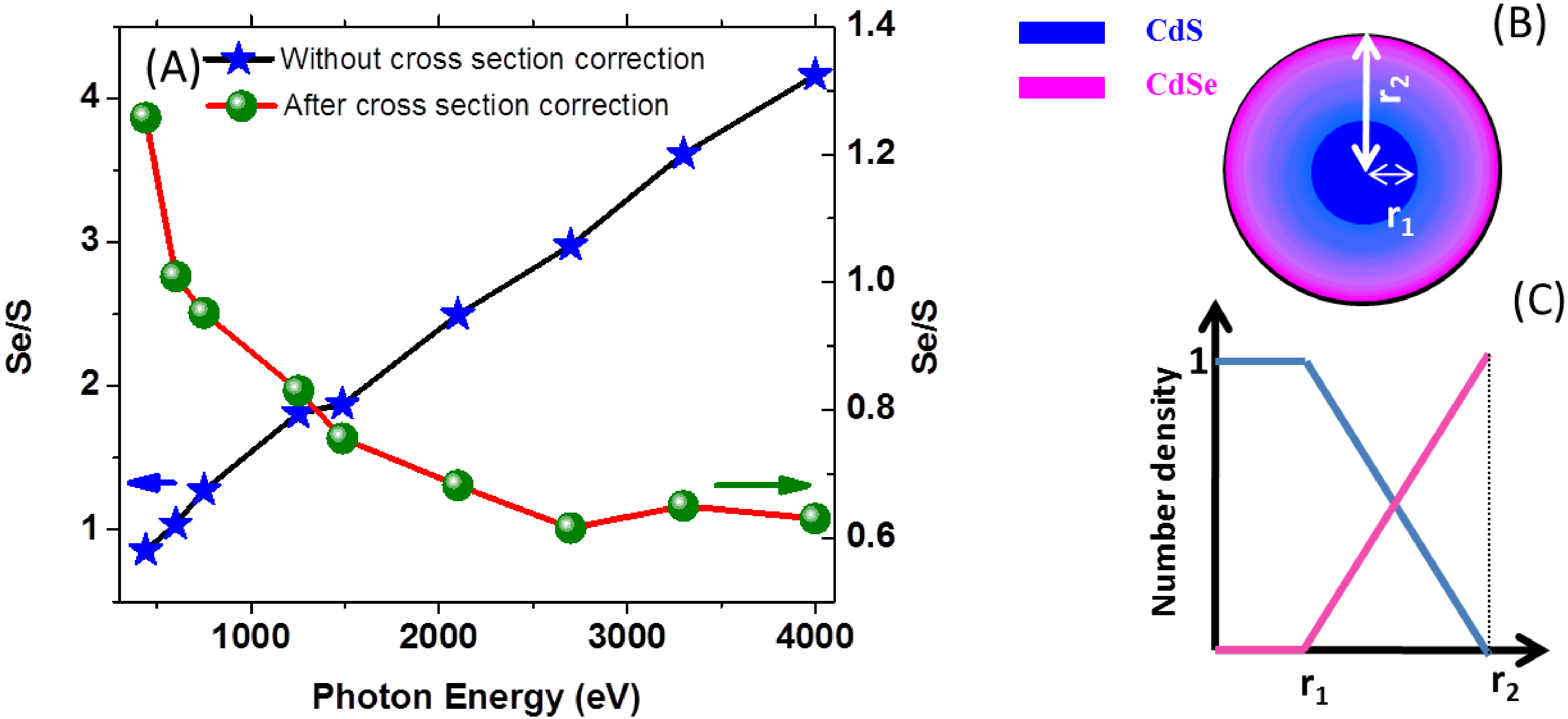


Figure 2. (A) *Photo emission spectra of S 2p and Se 3p core levels collected at various photon energies for the inverted CdS/CdSe core-shell sample.* (B)-(G) *shows the de-convolution of the experimental spectra (black open circles) to different components namely Se 3p's (blue) S 2p's (Olive) and Se 3p-surface (Magenta). Red solid lines are overall simulated spectra.*

From Bangalore: Sumanta Mukherjee, Abhijit Hazarika, D D Sarma
From UK: Ahmed L. Abdelhady, Azad Malik, P. O'Brien
Hike Beam line: Mihaela Gorgoi, O Karis
Italy Beamline: Pralay K. Santra,

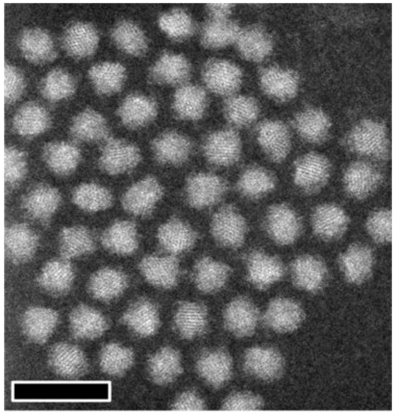


Variation of relative Intensity of S 2p to Se 3p at different photon energies. Blue Stars are before cross section correction and Olive spheres are after cross section correction. (B) *The modeled structure giving the best agreement with the experimentally obtained results of XPS, TEM and ICP.* (C) *Modelled structure of CdSeS generated to simulate the experimentally obtained intensity ratio.* (D) *Experimental intensity ratio of S/Se and S/Cd (Black and Red star) compared with the simulated ratio's (Black and Red star) for the modeled structure.*



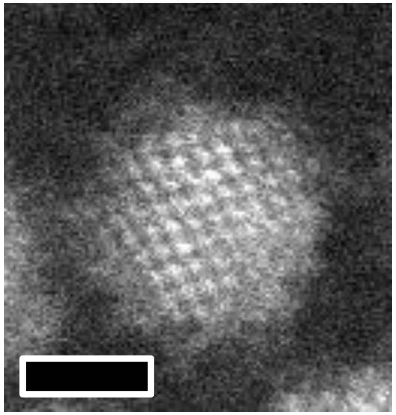
(A) *Variation of relative Intensity of Se 3p to S 2p at different photon energies. Blue stars are before cross section correction and Olive spheres are after cross section correction.* (B) *The modeled structure giving the best agreement with the experimentally obtained results from XPS, TEM and ICP.* (C) *Variation of number density of S (Blue line) and Se (Magenta line) as a function of radius of the nano particle for the best fitted structure.*

TEM images

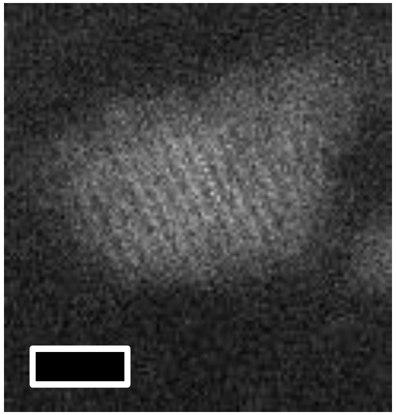


CdSe

(Scale bar - 10nm)

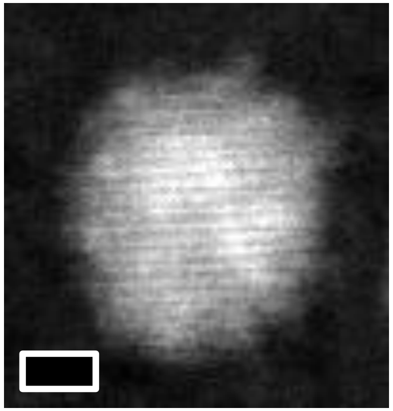


CdSe



CdSe/CdTe

(Scale bar - 2nm)



CdSe/CdTe/CdS

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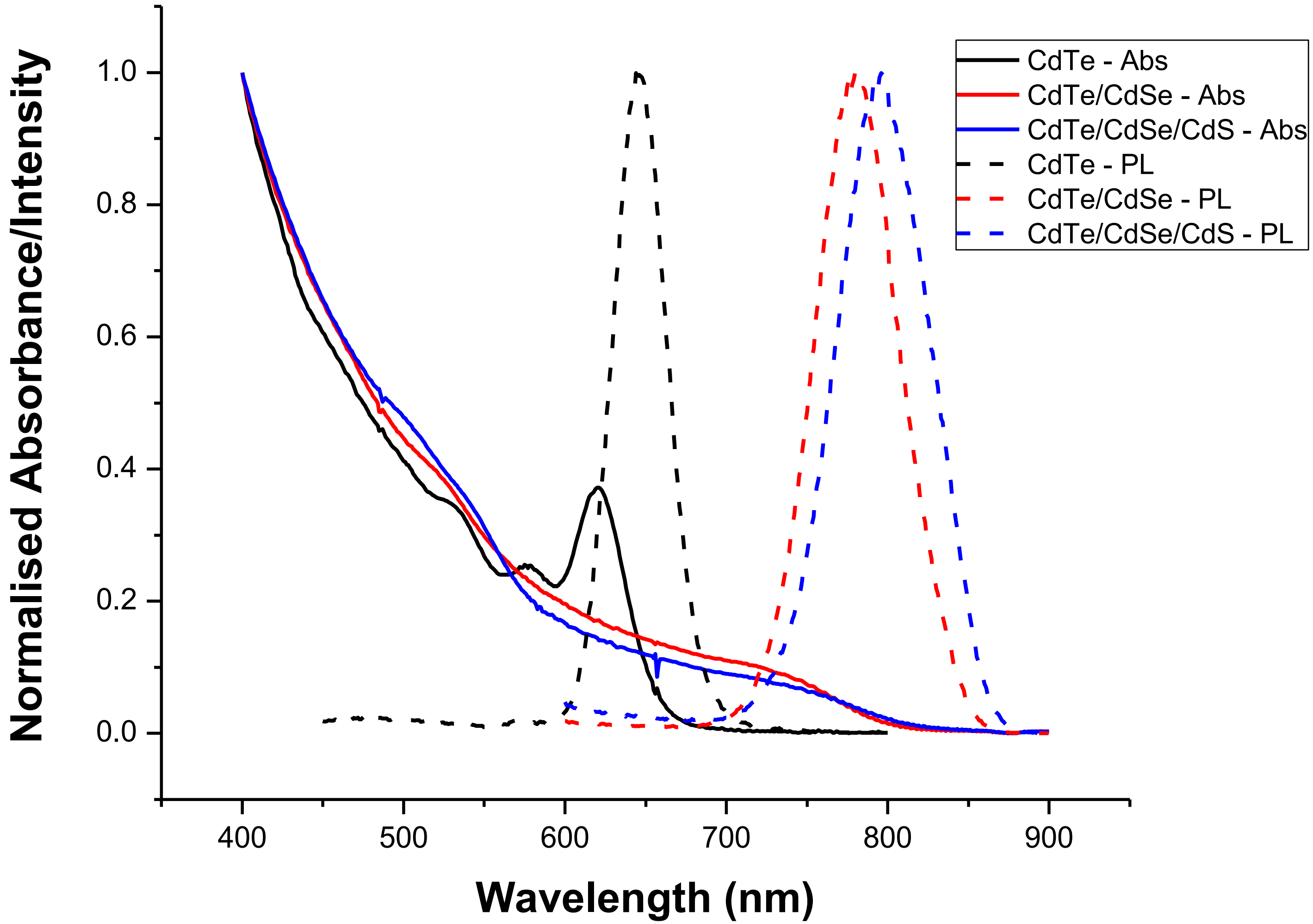
Synthesis of CdTe/CdSe/CdS



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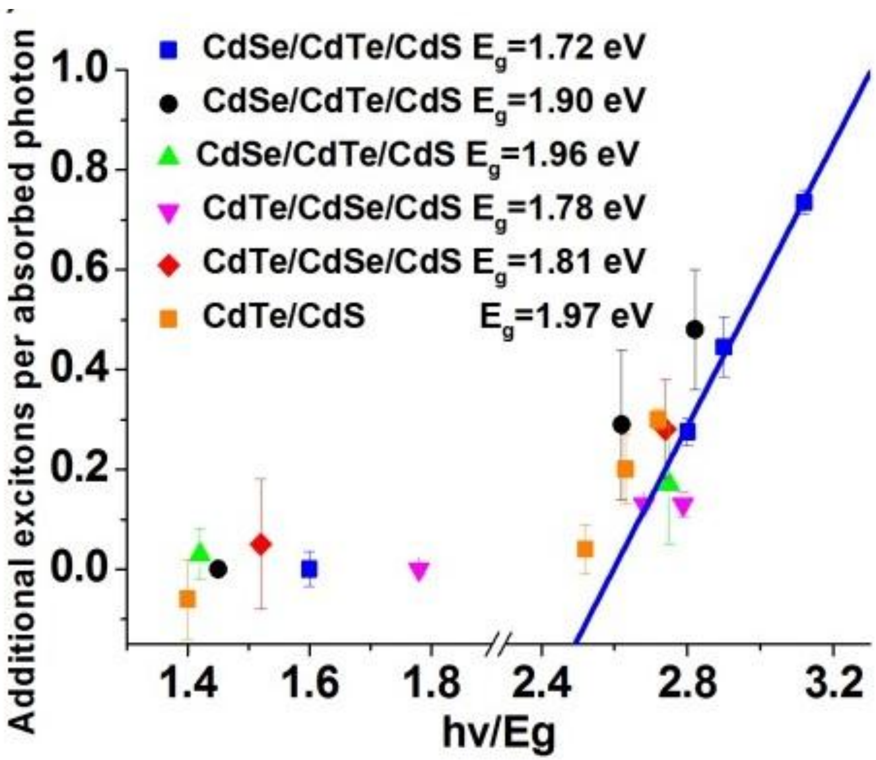
Multiple Exciton Generation

- Quantum Yield measured comparing low power values
- MEG threshold comparable to literature values
- Slope efficiency nearly three times greater than anything reported



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