Solution Synthesis of Nanoparticles and Quantum Dots

Never Stand Still

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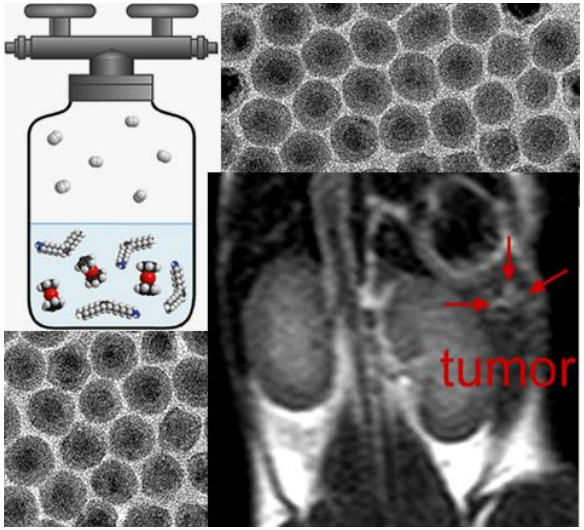
School of Chemistry,

Mark Wainwright Analytical Centre,

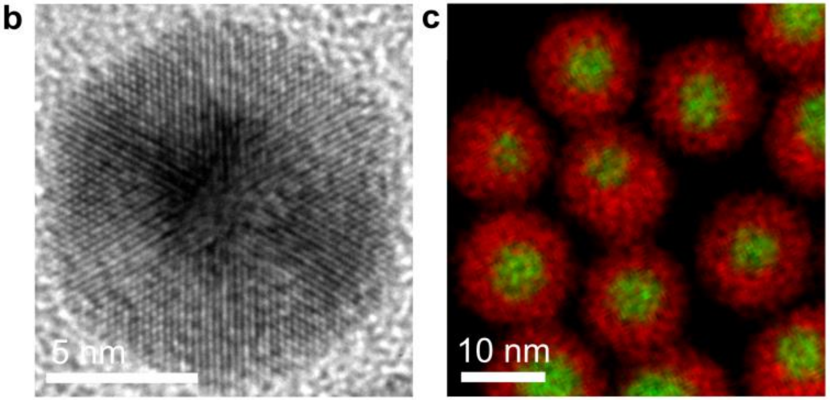
Australian Centre for NanoMedicine

Nanoparticles Synthesis

- Magnetic
  - Fe, Fe_3O_4, Fe_3S_4

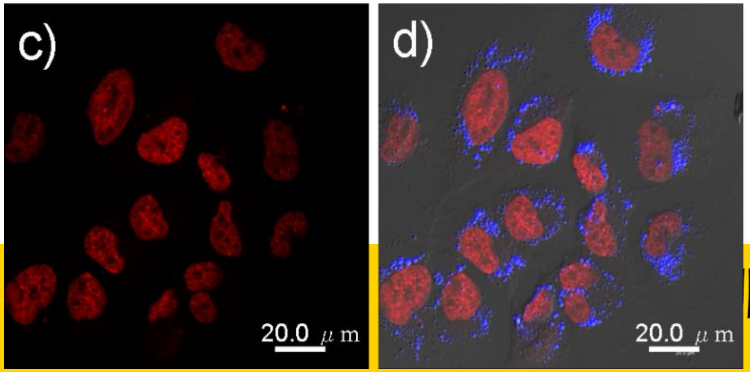


- Metals,
  - Pd@Au, Au@Pd, Ru, Pt, Pd, Ni



- Quantum dots,
  - IV Si and Ge,

IV-VI SnS, SnTe



Two methods we make particles in solution

Decomposition

heat

Fe precursor → Fe

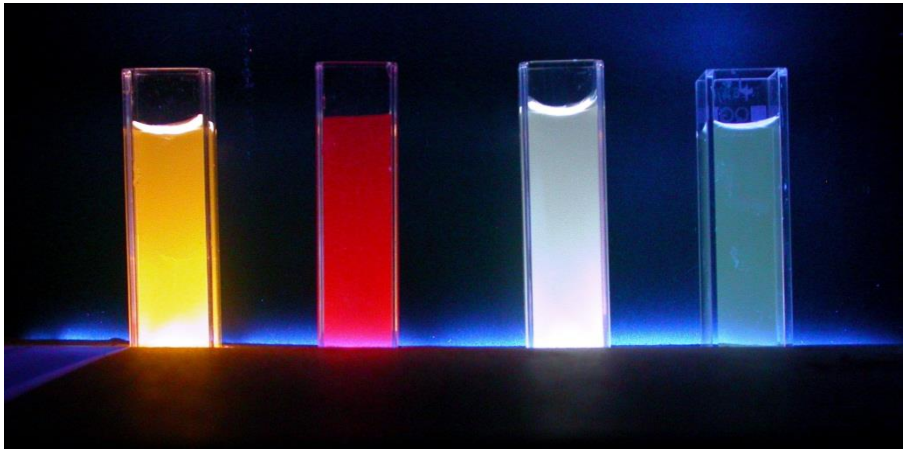
Fisher Porter bottle - 1 hour to 3 days (hot injection in seconds)

Surfactant → size and shape control.

Silicon and Germanium Quantum Dots

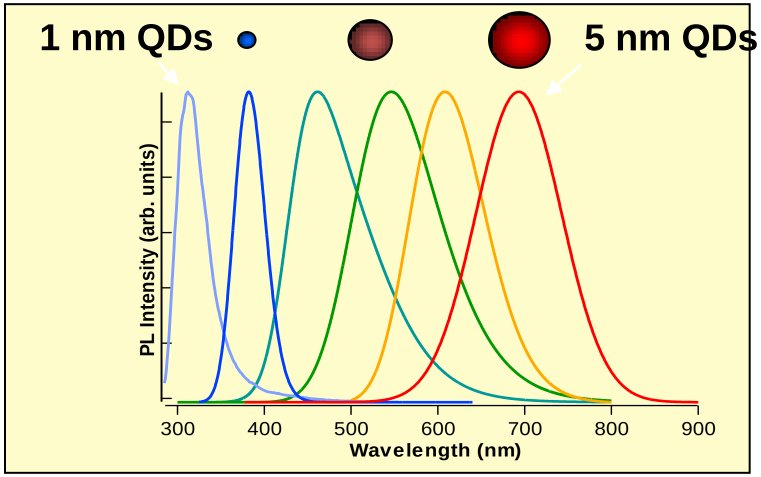
Properties of Quantum dots

- Sharper emission spectra → Purer colours.
- Stability.
- Size selective emission



Applications

- ◆ Physical - displays
- ◆ Biological - imaging

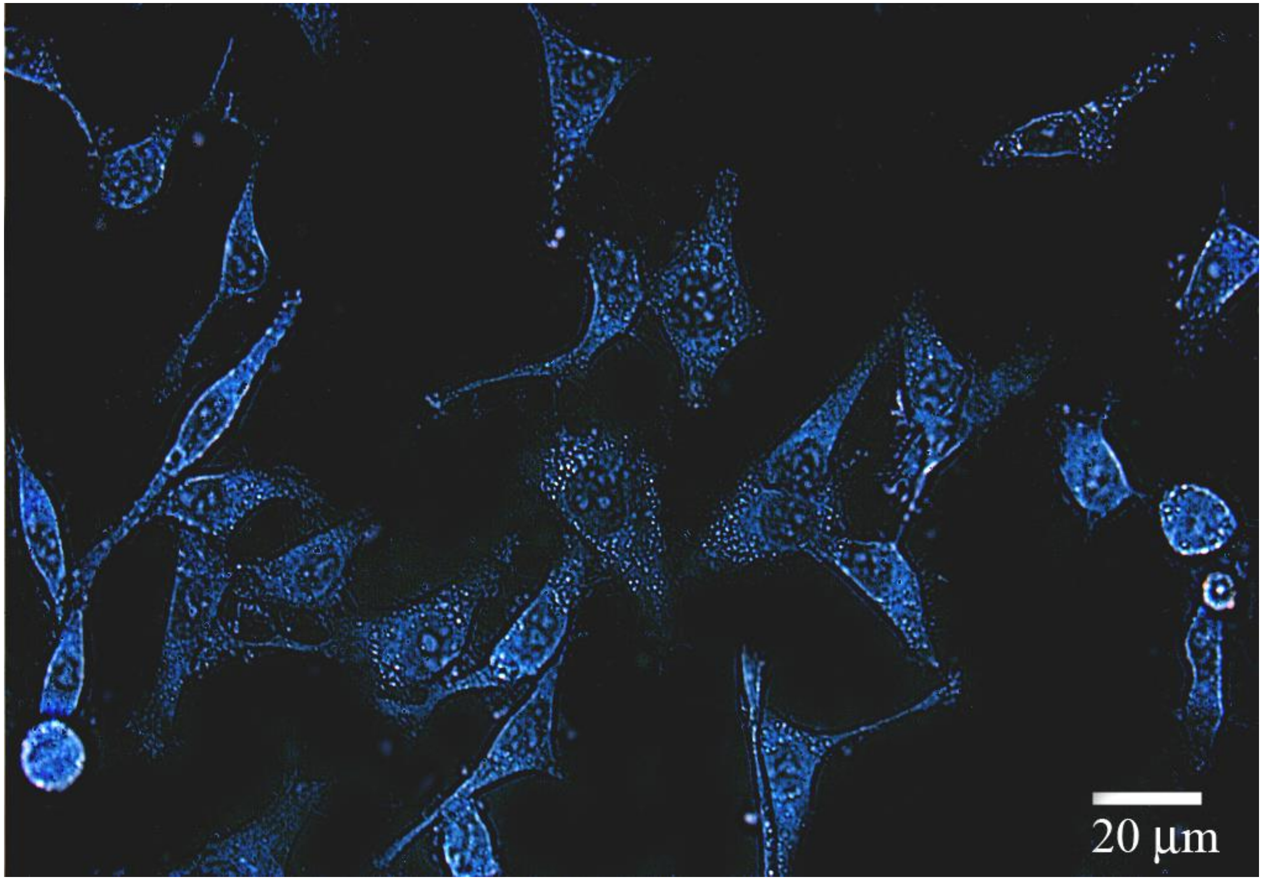


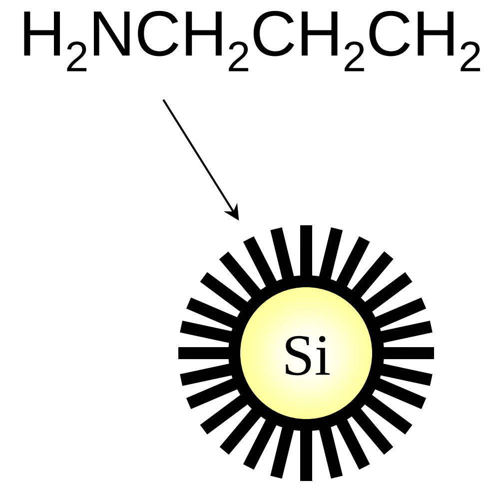
Properties of Silicon nanoparticles

- Are CdSe particles toxic? *(Nano Lett.*,4, 2004, 11 Derfus *et al*).

- Si and Ge nanoparticles as an alternative.
- Less-toxic & environmentally friendly.

Silicon quantum dots



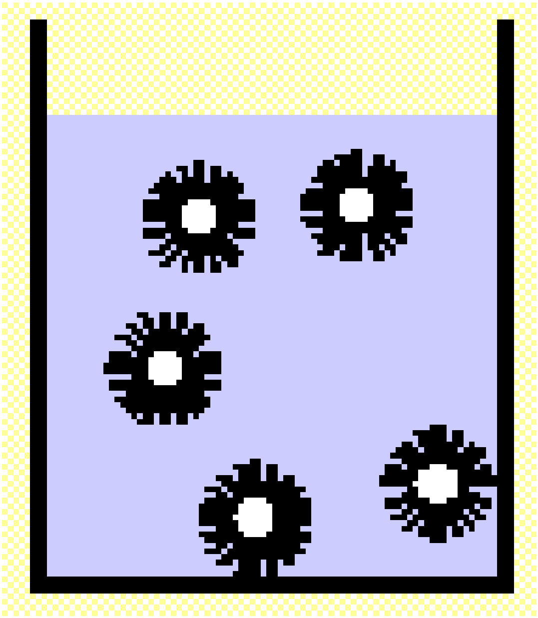


- Low toxicity
- Si dots and HeLa cells (with Kenji Yamamoto International Medical Center Japan).

R. D. Tilley and K. Yamamoto, *Adv. Mater.*, 18, 2053 (2006).

Micelle synthesis of Si and Ge nanocrystals

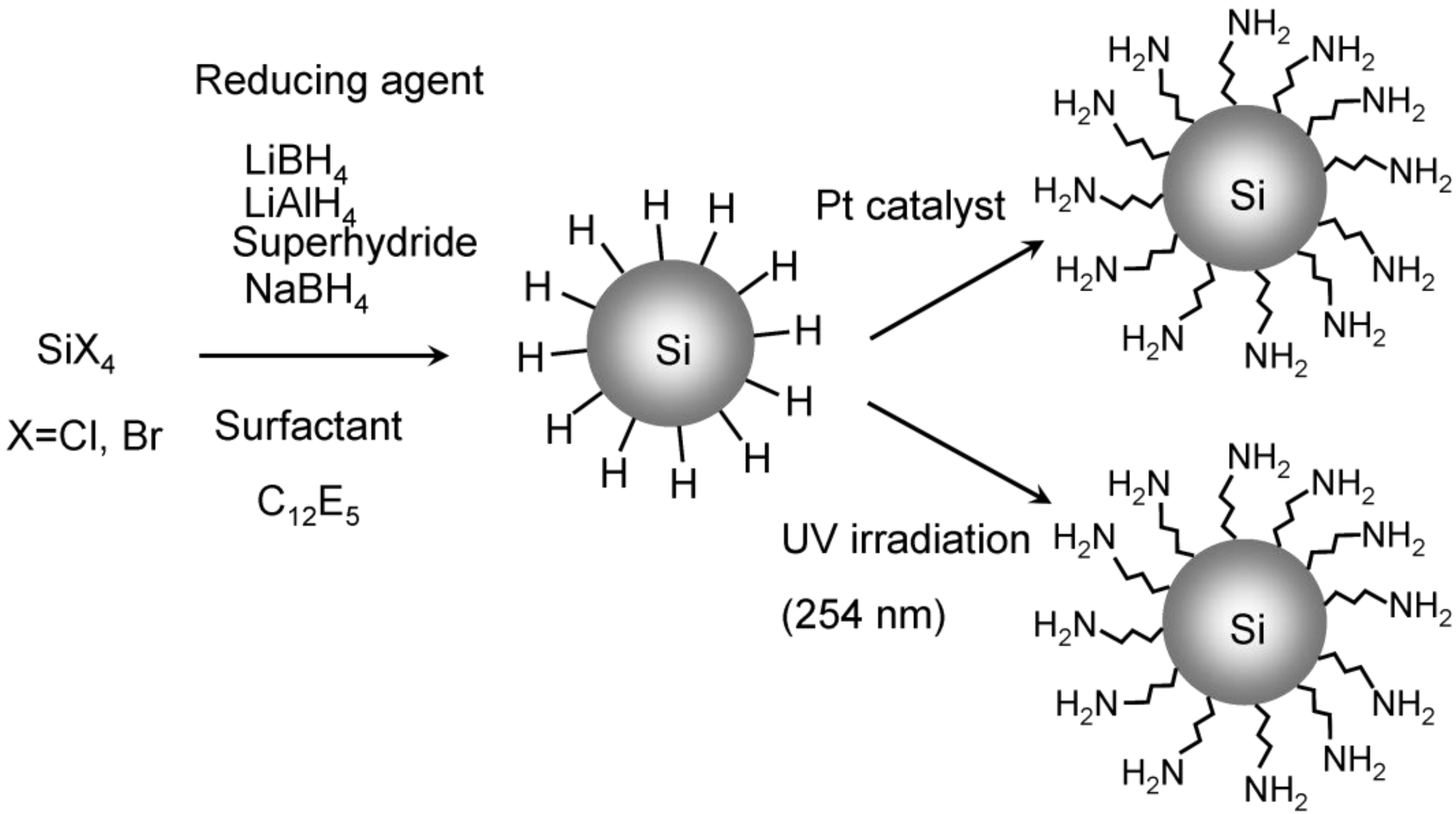
- $SiCl_4$ or $GeCl_4$ + $LiAlH_4$, Si(IV) → Si(0).
- Use Glove Box - O_2 and H_2O free synthesis - silica SiO_2 formation.



$SiCl_4$ + surfactant (TOAB)

J. H. Warner, A. Hoshino, K. Yamamoto, R. D. Tilley Agnew. Chem. Int. Ed. 2005, 44, 4550-4554.

Quantum Dots



A. Shiohara, S. Prabakar, A. Faramus, C-Y. Hsu, P-S Lai, P. T. Northcote, R. D. Tilley *Nanoscale,* 3, 3364-3370 (2011).

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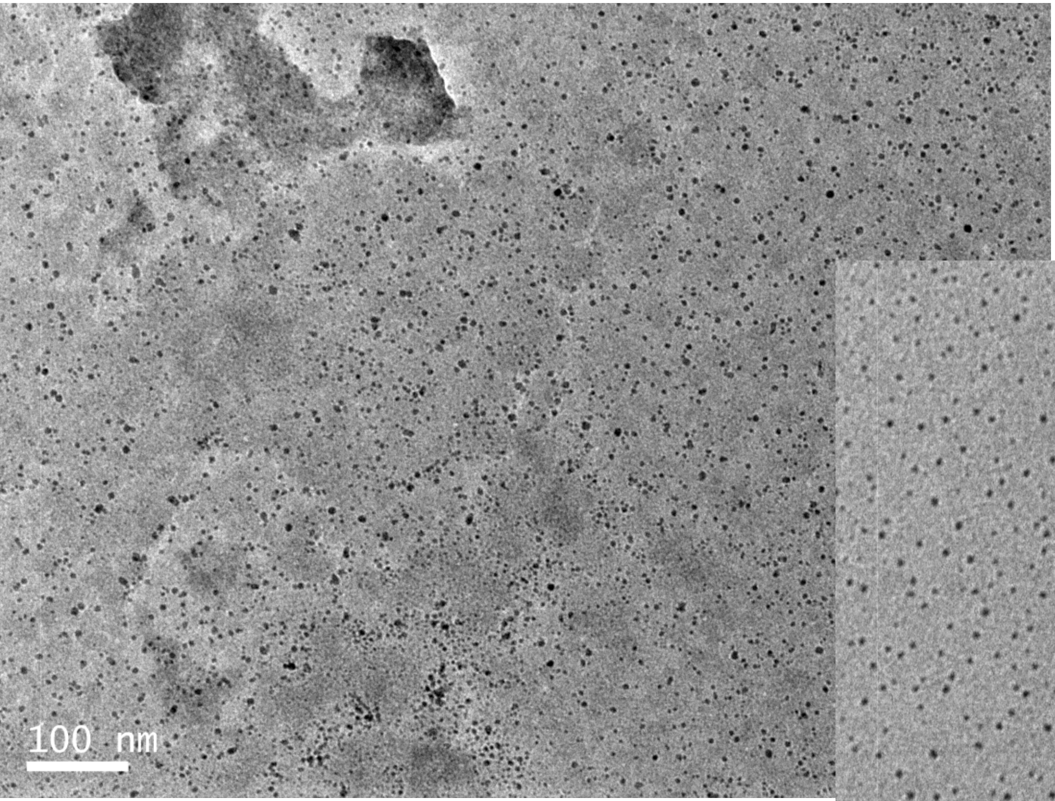
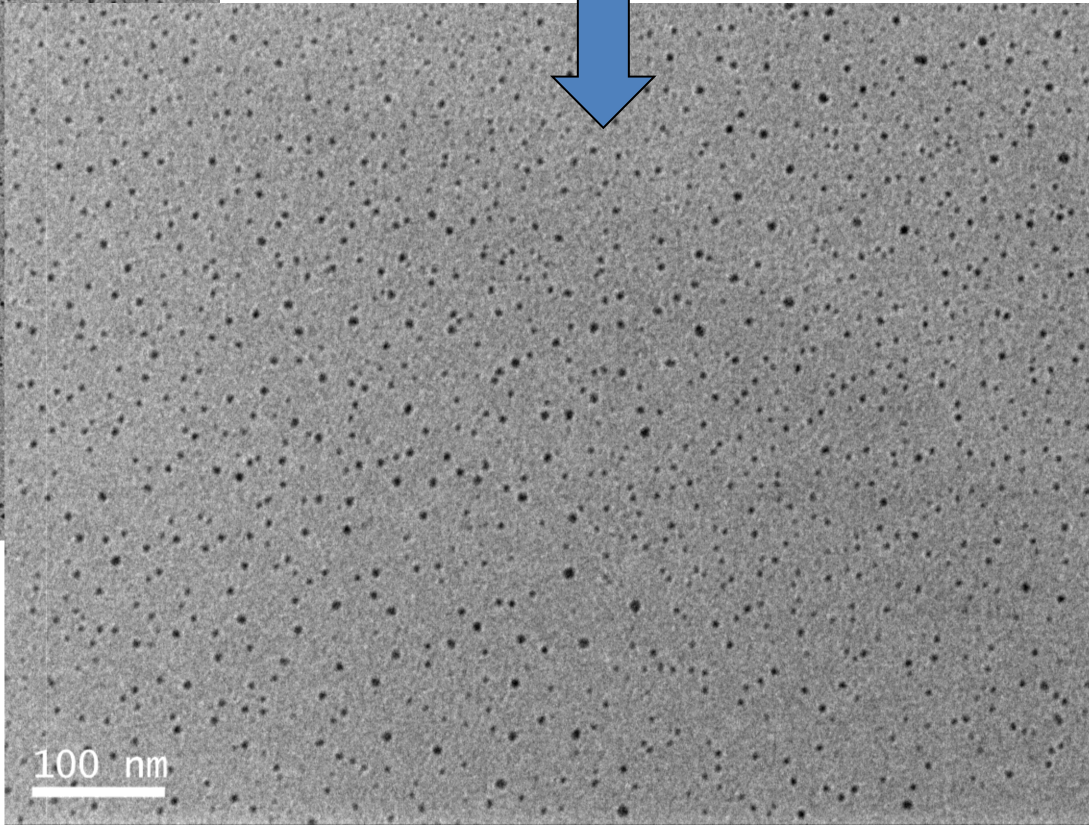
Purification



Before

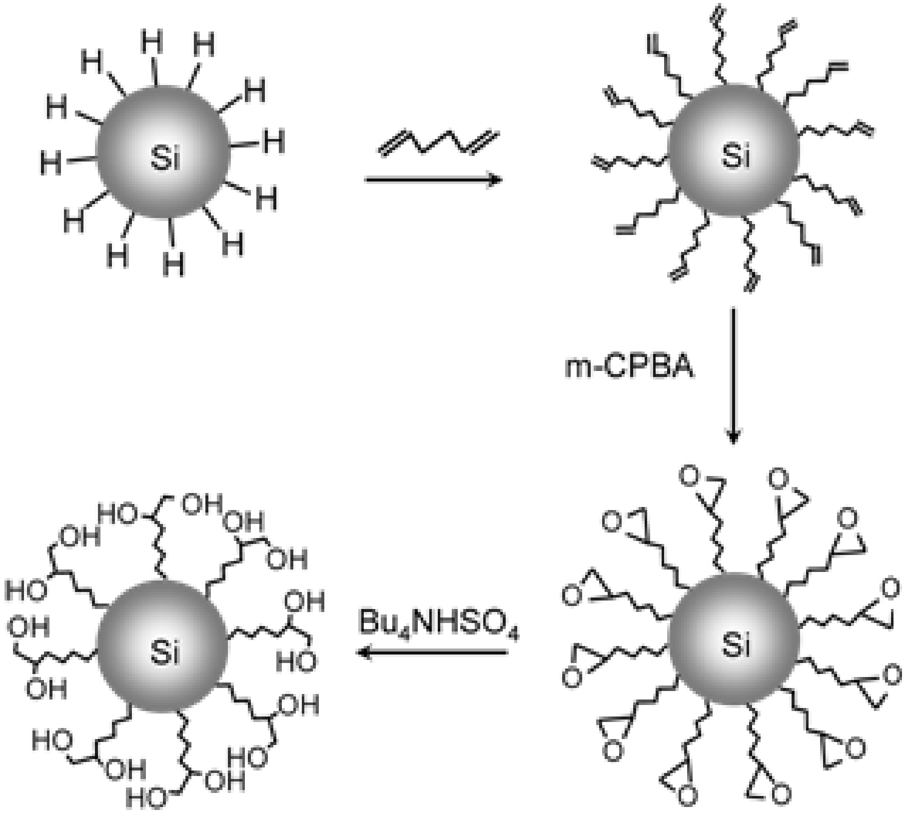
After

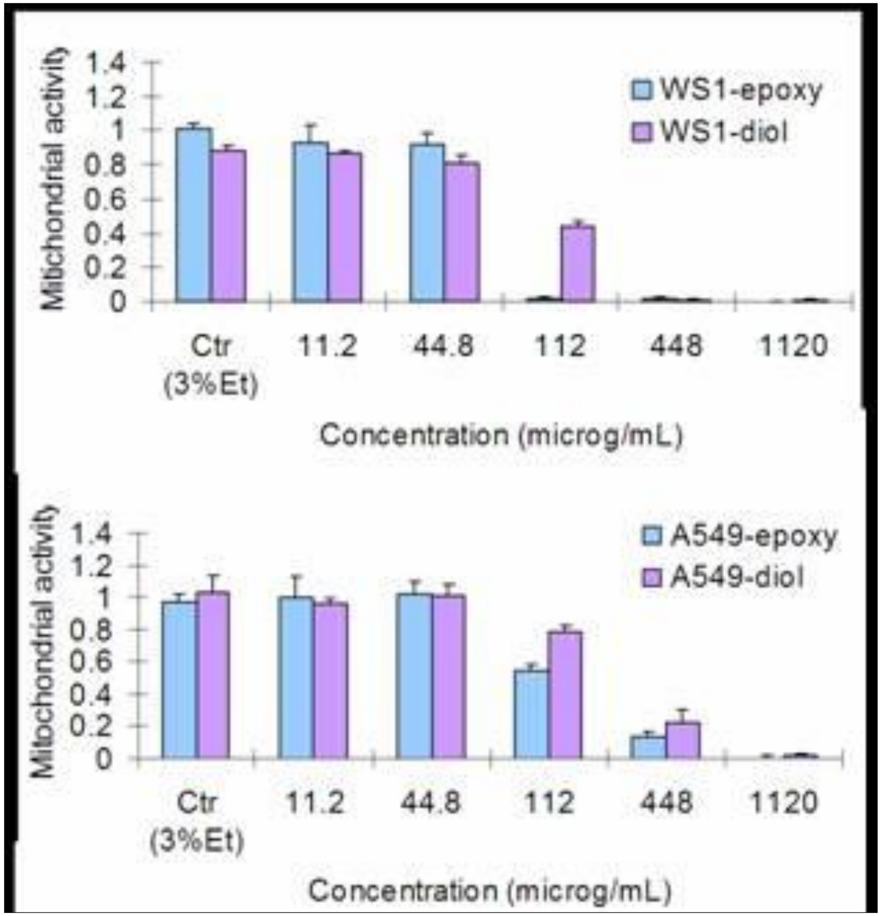


- Bohr radius about 4 nm
- Size selective column chromatography

A. Shiohara, S. Prabakar, A. Faramus, C-Y. Hsu, P-S Lai, P. T. Northcote, R. D. Tilley *Nanoscale,* 3, 3364-3370 (2011).

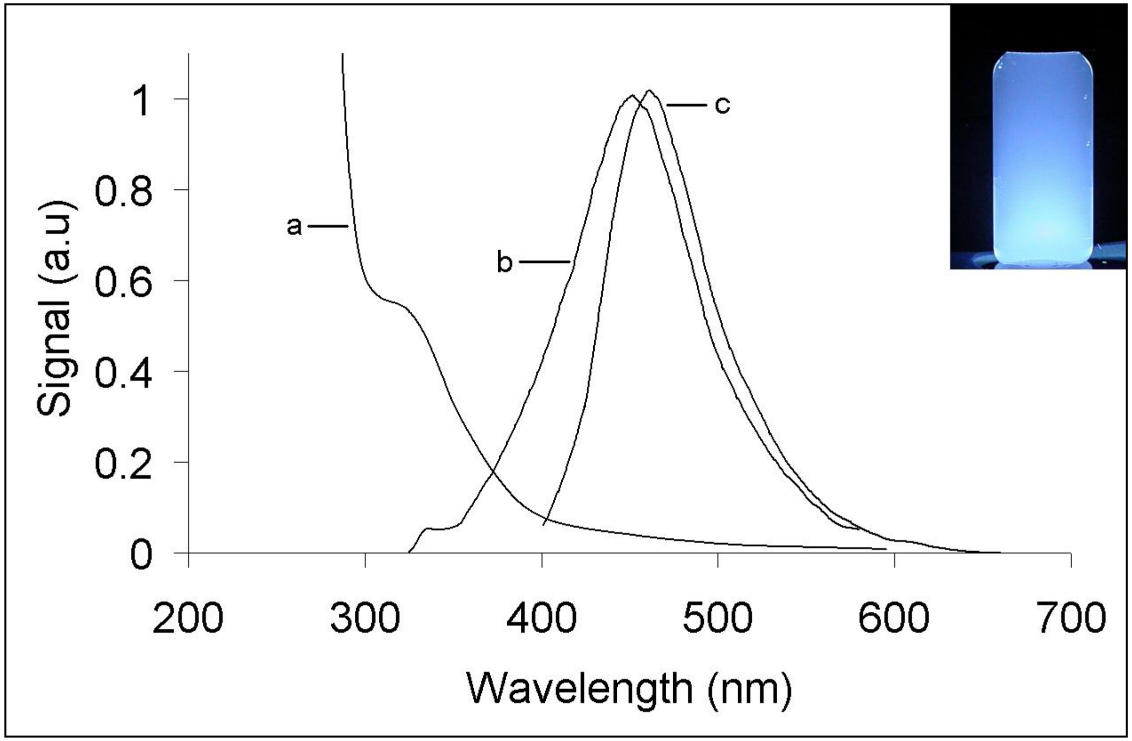
Problem for Oxygen containing species





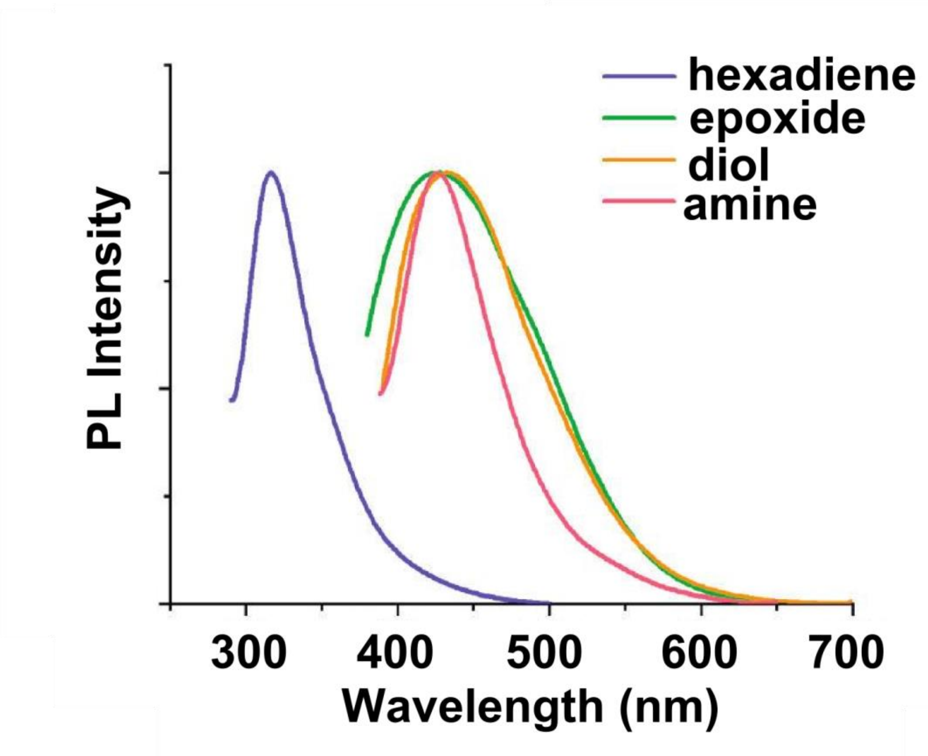
A. Shiohara, S. Prabakar, S Hanada, K Fujioka, K Yamamoto, P. Northcote, R D Tilley s *JACS,* 132, 248–253 (2010).

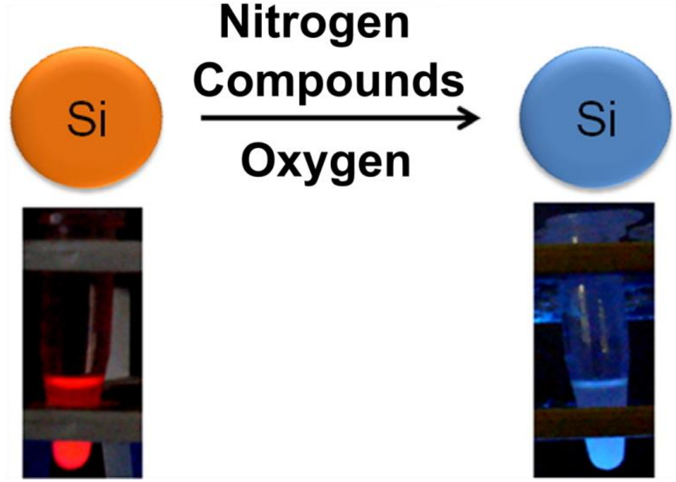
PL allylamine particles



- Bohr radius about 4 nm.
- 480nm emission peak - Vial of silicon nanocrystals.
- Quantum yield 10 %

Surface matters

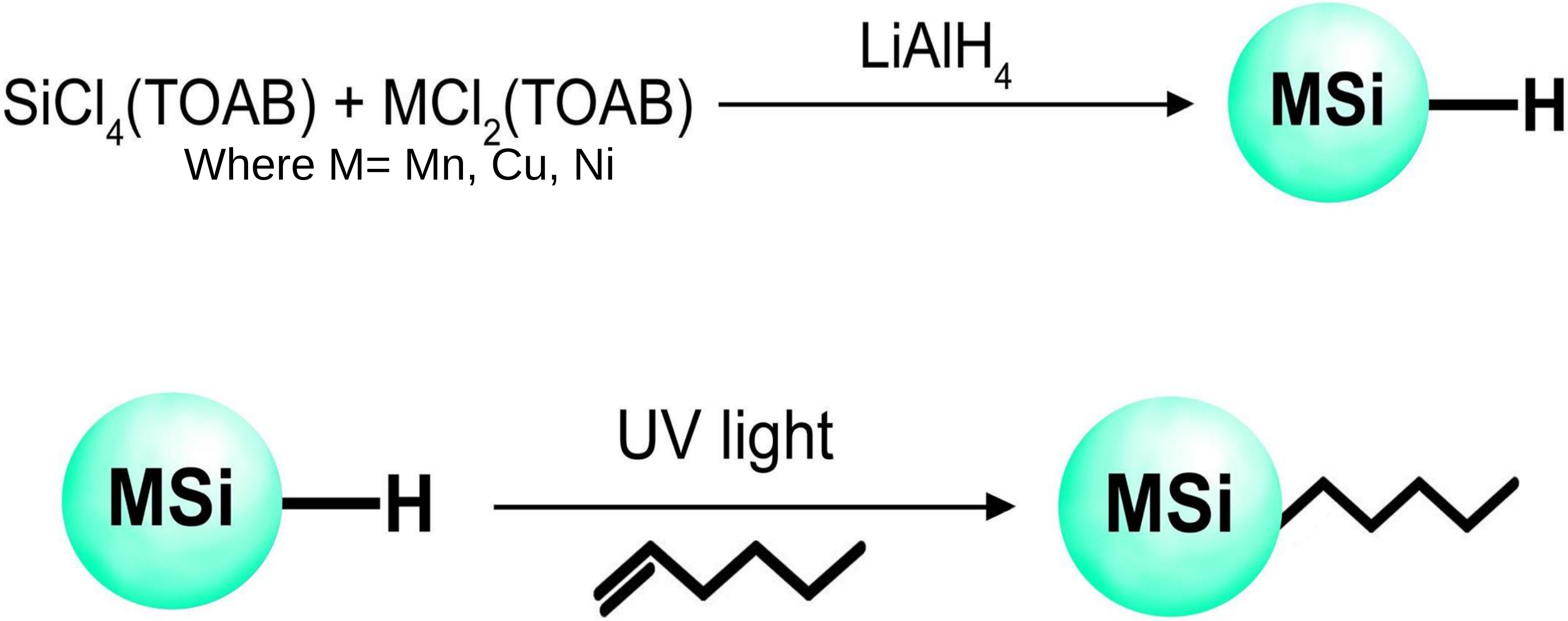




With, Jonathan G. C. Veinot and Susan M. Kauzlarich, ACS Nano, 2676–2685, 2013

Si QDs with Mn Ni and Cu Doping

- Dopant level at 1 % relative to Si



B. F. P. McVey and co-workers *Journal of Physical Chemistry Letters*, *6*, 1573-1576 (2015).

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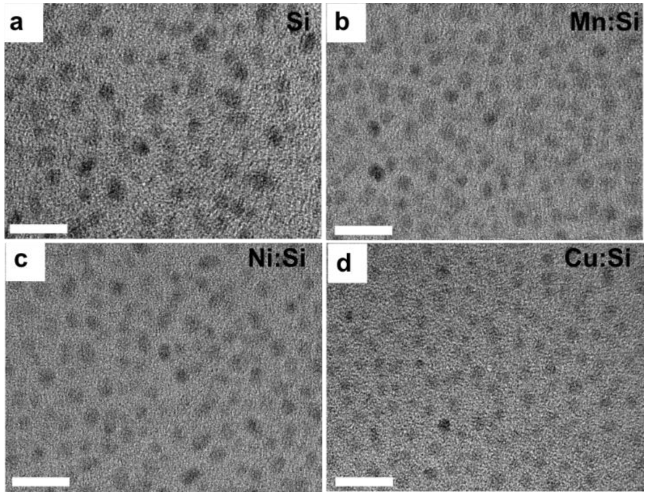
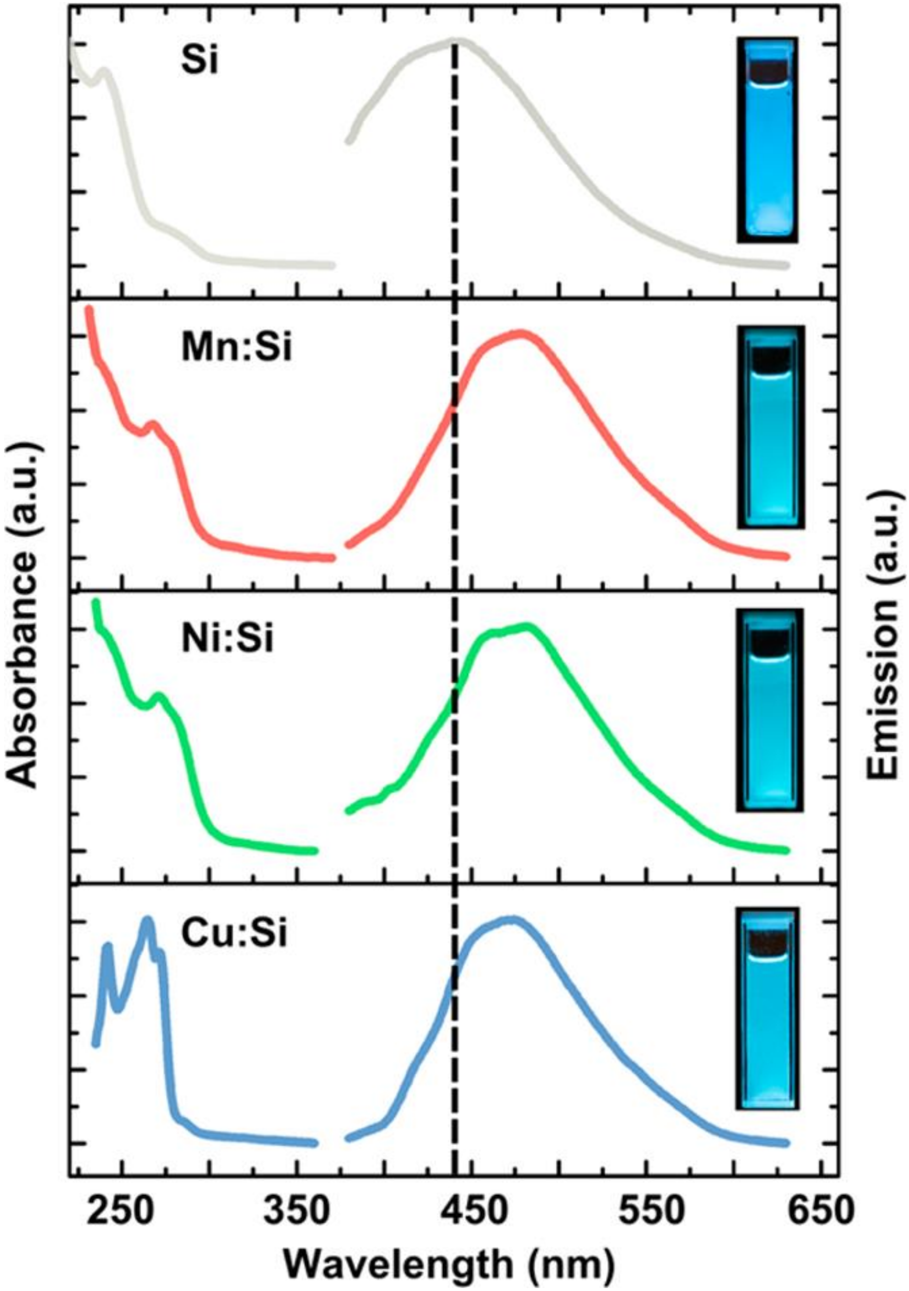
Doped Si QDs

- Mn and Ni doped Si QDs PL
  - Si (443 nm)
  - Mn:Si (475 nm)
  - Ni:Si (485 nm)
  - Redshift ~ 50 nm





B. F. P. McVey and co-workers *Journal of Physical Chemistry Letters*, *6*, 1573-1576 (2015).

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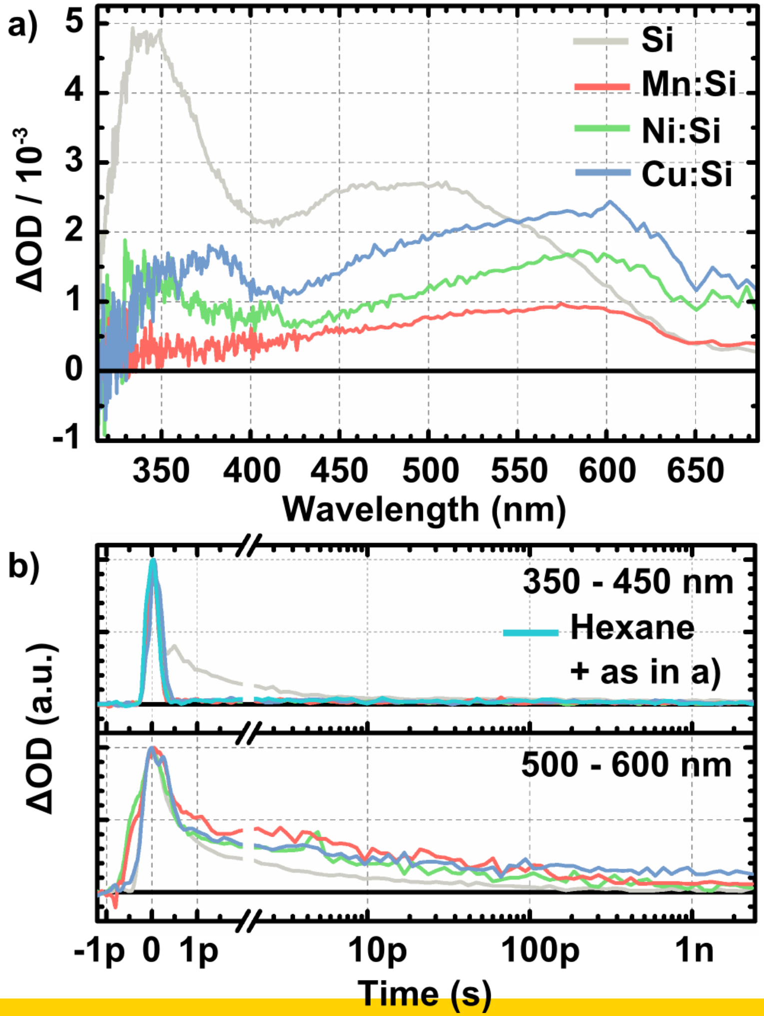
Optical properties of metal doped Si NCs



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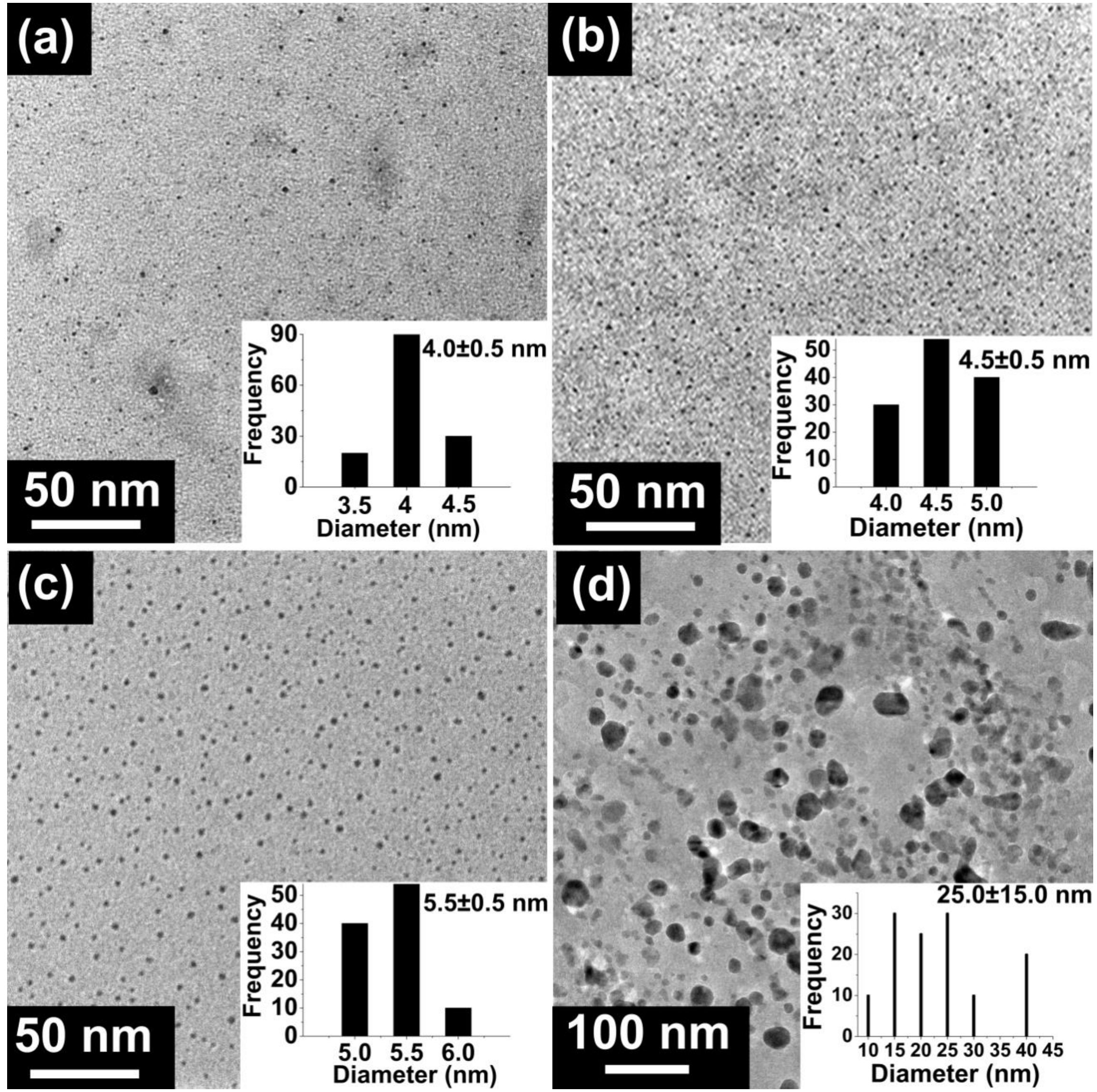
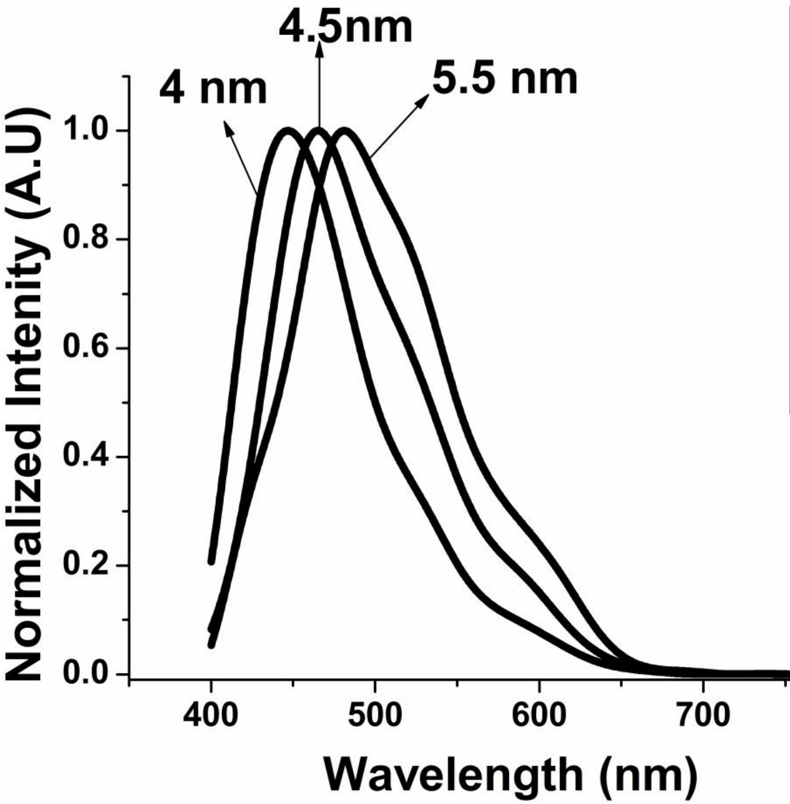
Germanium Quantum Dots

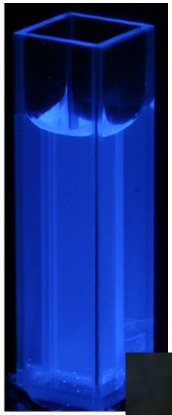
- $LiAlH_4$
- $LiBH_4$
- $LiBEt_3H$
- $NaBH_4$

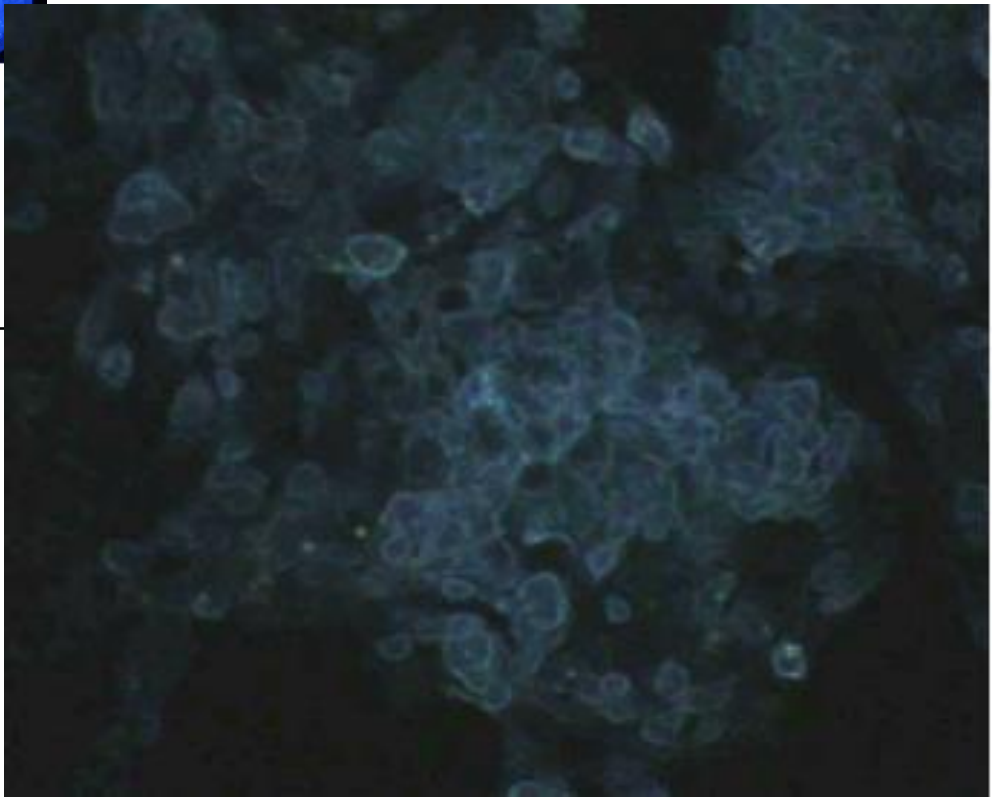


S. Prabakar, A. Shiohara, S Hanada, K Fujioka, K Yamamoto, R D Tilley *Chem. Mater.*, 22, 482–486 (2010).

Germanium Quantum Dots



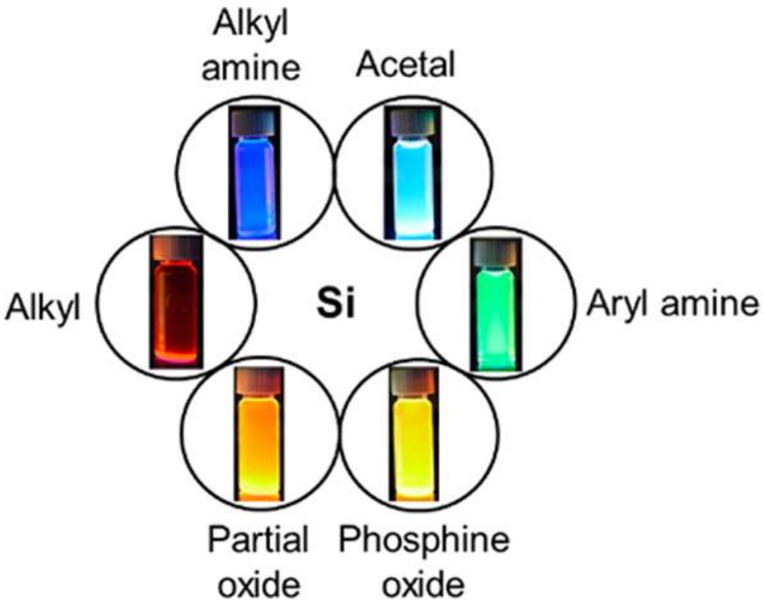


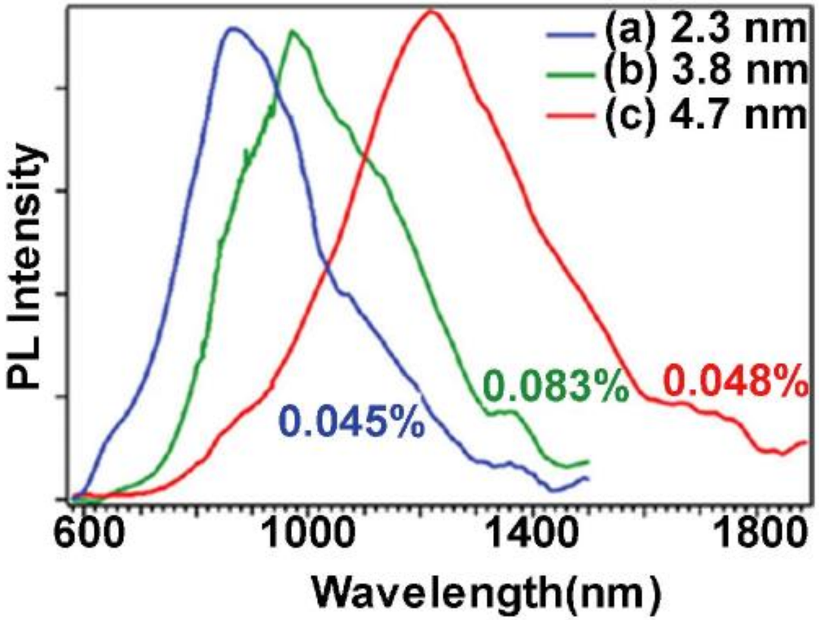


S. Prabakar and coworkers *Chem. Mater*, 22, 482–486 (2010).

Silicon and Germanium Nanocrystals (Si and Ge NCs)

- Unique Optical Properties
- Low Toxicity
- Low quantum yields 10%.



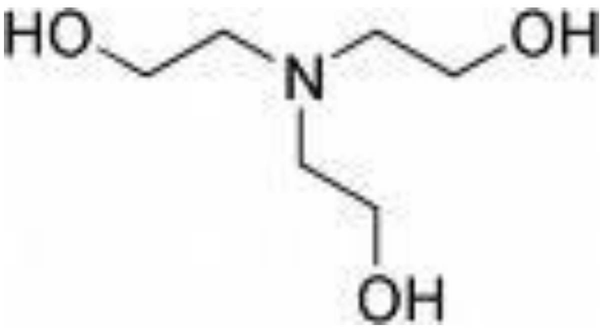


M. Dasog, G. B. De Los Reyes, L. V. Titova, F. A. Hergmann, J. G. C. Veinot *ACS Nano* 2014, *8*, 9636-9648
D. A. Ruddy, J. C. Johnson, E. R. Smith, N. R. Neale *ACS Nano* 2010, *47*, 7459-7465.

SnS
Quantum dots

SnS,

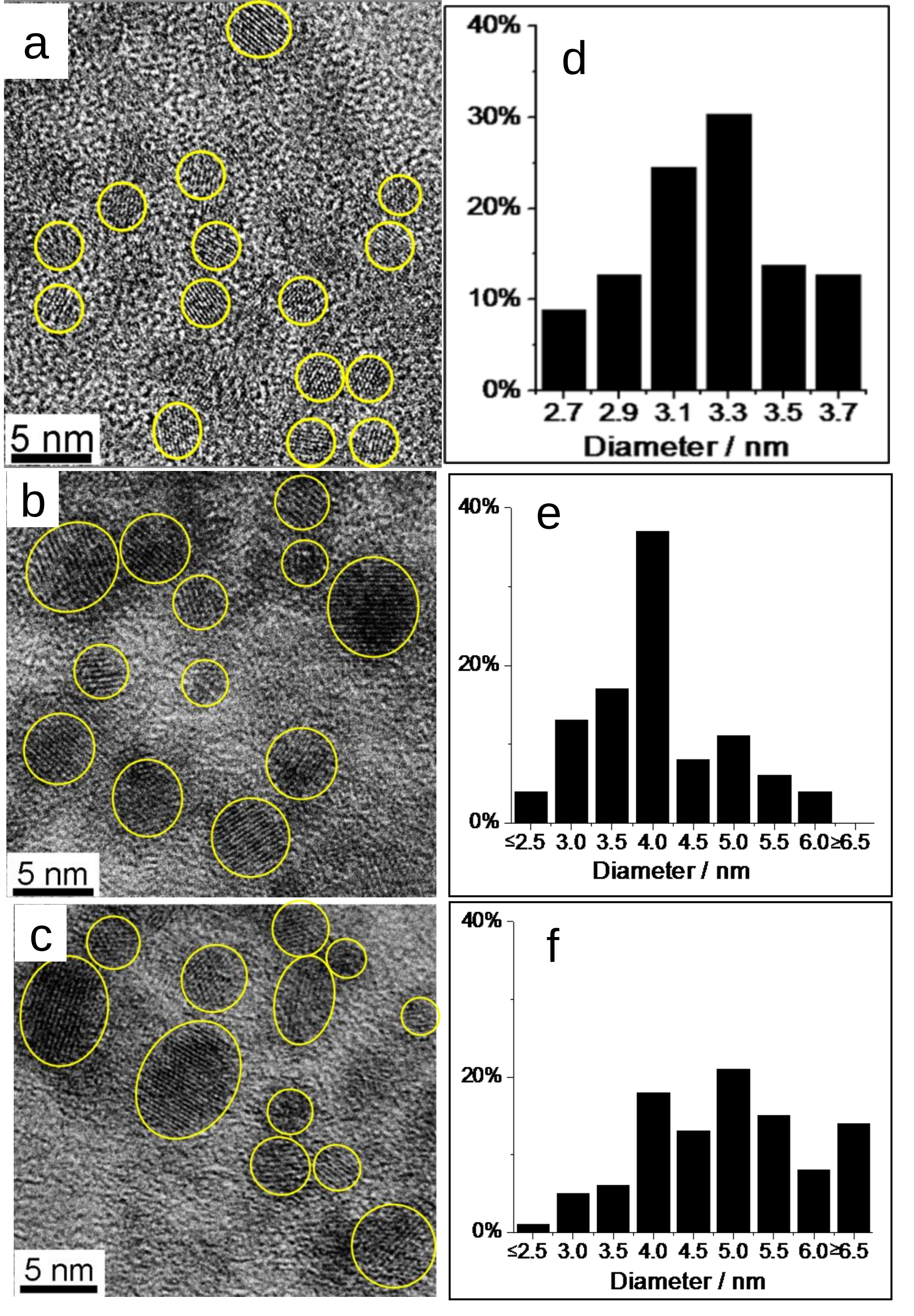
- $SnBr_2$ and Na_2S
- With ethanolamines
  - 3 hydroxyl groups
  - 2 hydroxyl groups
  - 1 hydroxyl group



3 hydroxyl groups

2 hydroxyl groups

1 hydroxyl group

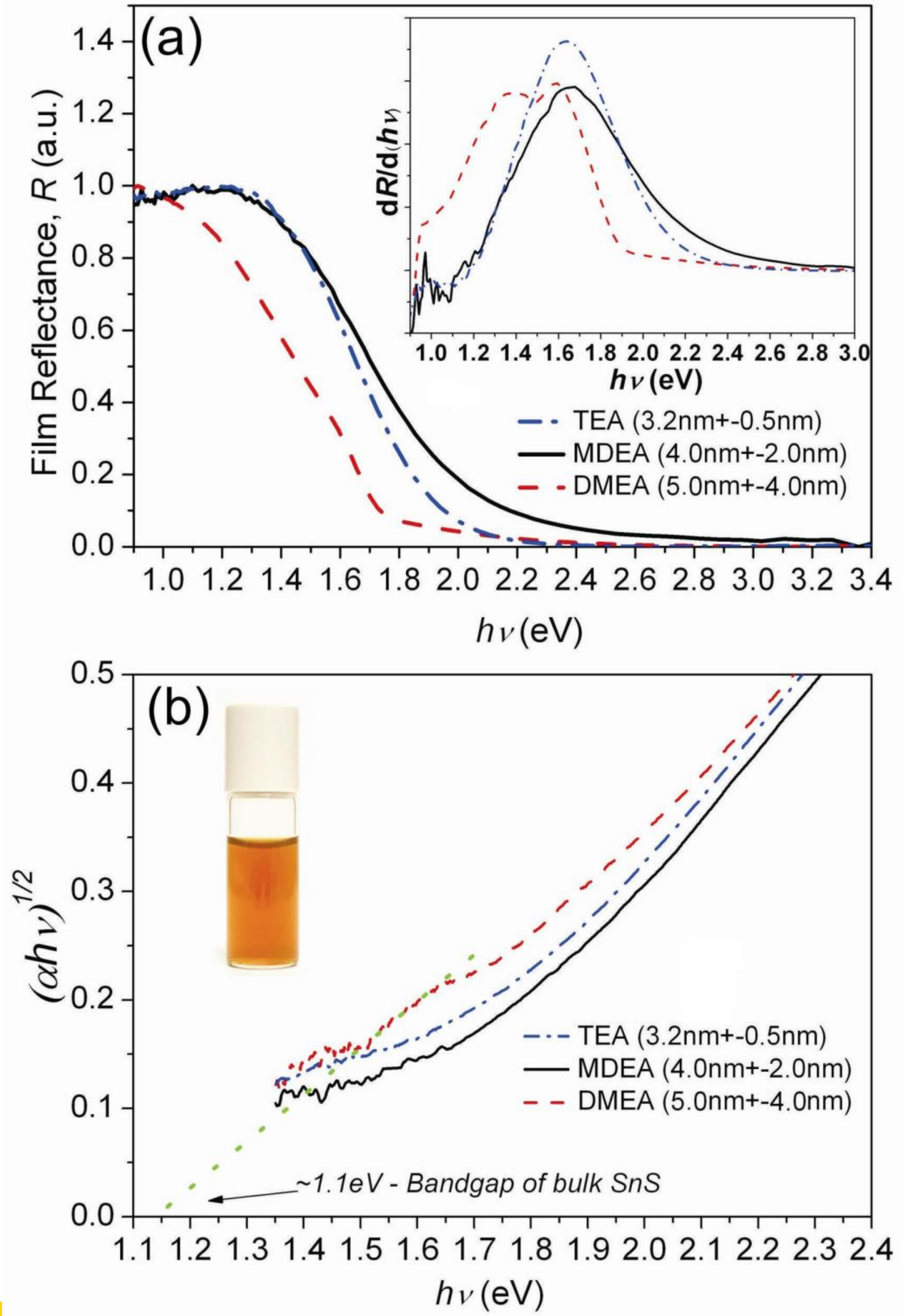


X. Ying, C. W. Bumby, N. Al-Salim and R. D. Tilley *JACS 131,* 15990 (2009).

SnS

- For indirect band gap semiconductor

absorption coefficient $\alpha^{0.5}$ $\propto$ photon energy $h\upsilon$

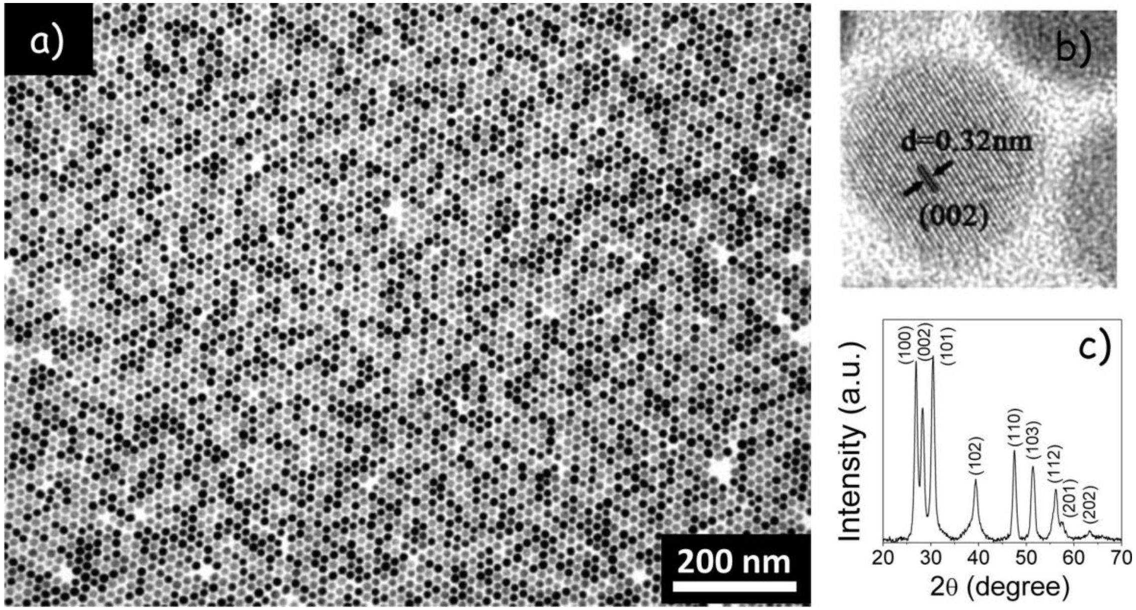


X. Ying, C. W. Bumby, N. Al-Salim and R. D. Tilley *JACS 131*, 15990 (2009).

CZTS
Quantum dots

Cu_2ZnSnS_4 NCs (CZTS NCs)

- Earth abundent



W. Wang, M. T. Winkler, O. Gunawan, T. K. Todorov, Y. Zhu, D. B. Mitzi *Adv. Energy Mater*. 2014, *4*, 1-5.

X. Yu, A. Shavel, X. An, Z. Luo, M. Ibanez, A. Cabot *J. Am. Chem. Soc*. 2014, *136*, 9236-9239

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Synthesis of CZTS NCs

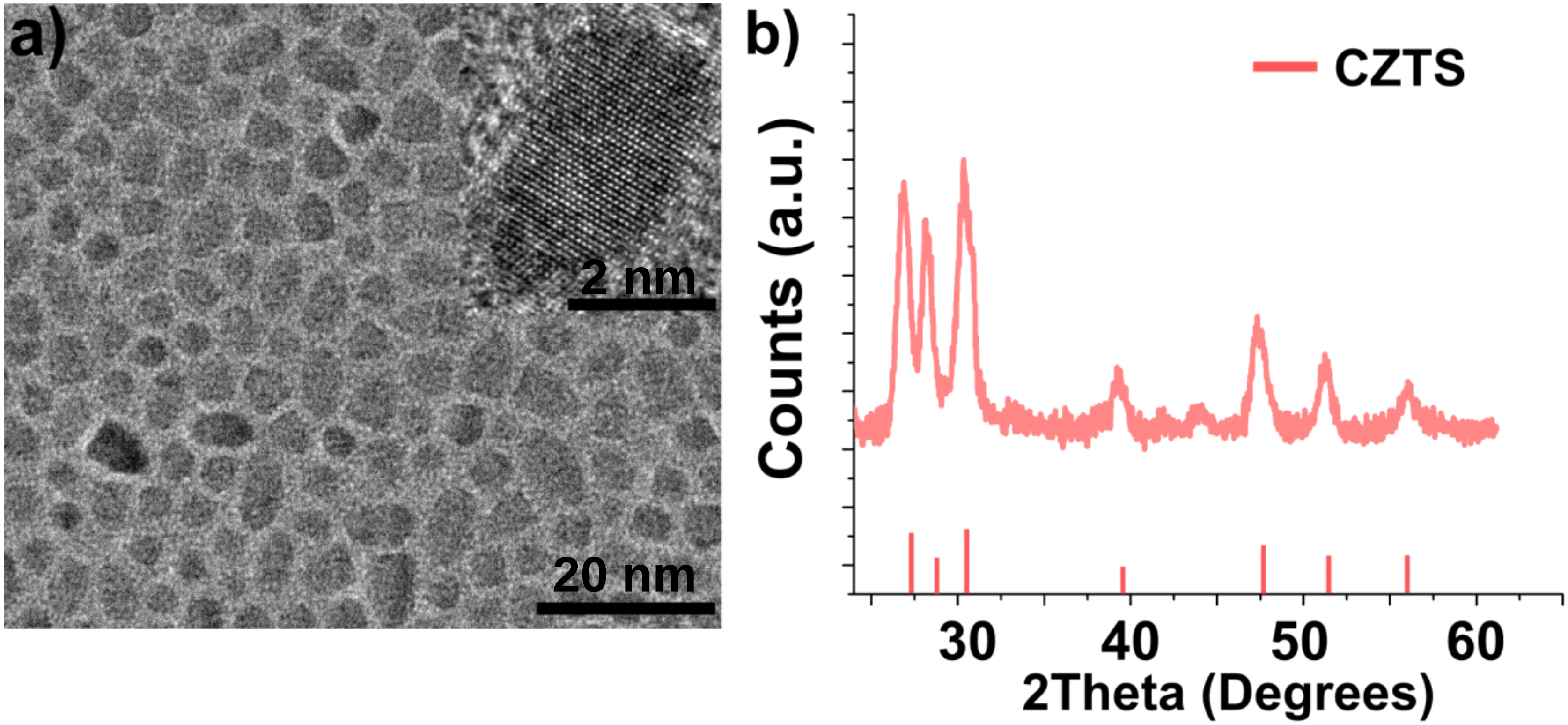
*

Metal precursors → **CZTS NCs**

Amine surfactants

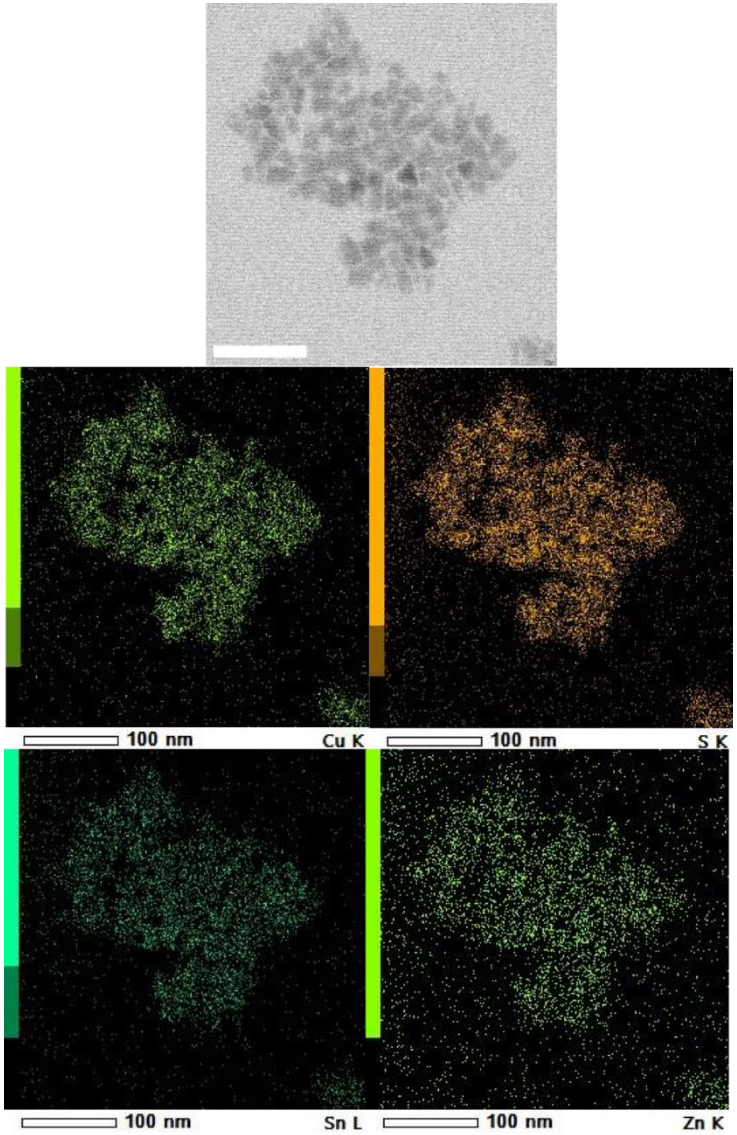
B. F. P. McVey *et al* Manuscript in Preparation

CZTS NCs



B. F. P. McVey *et al* Manuscript in Preparation

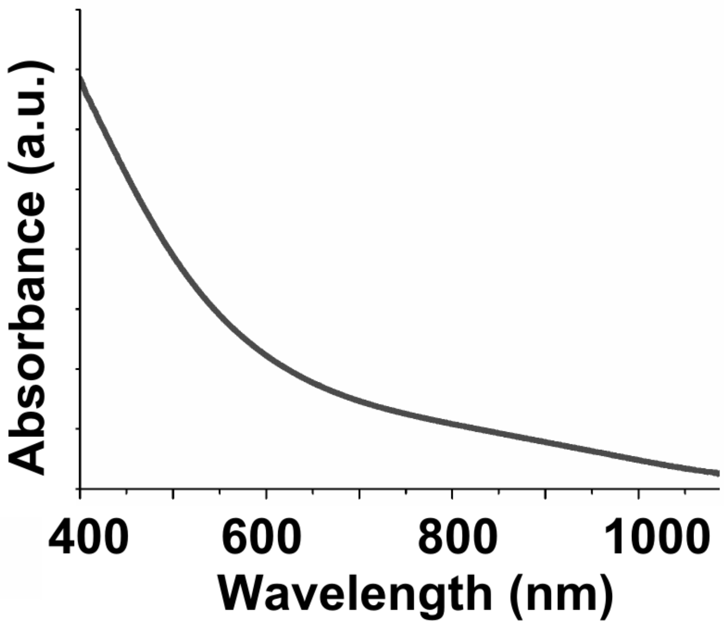
CZTS NCs

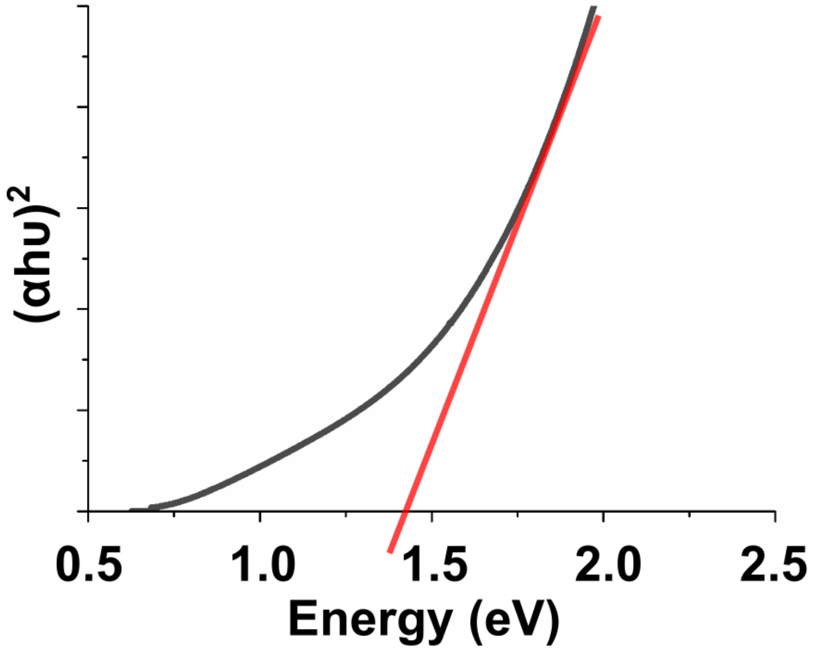


B. F. P. McVey *et al* Manuscript in Preparation

Optical Properties of CZTS NCs

Tune composition and optical properties
Collaboration

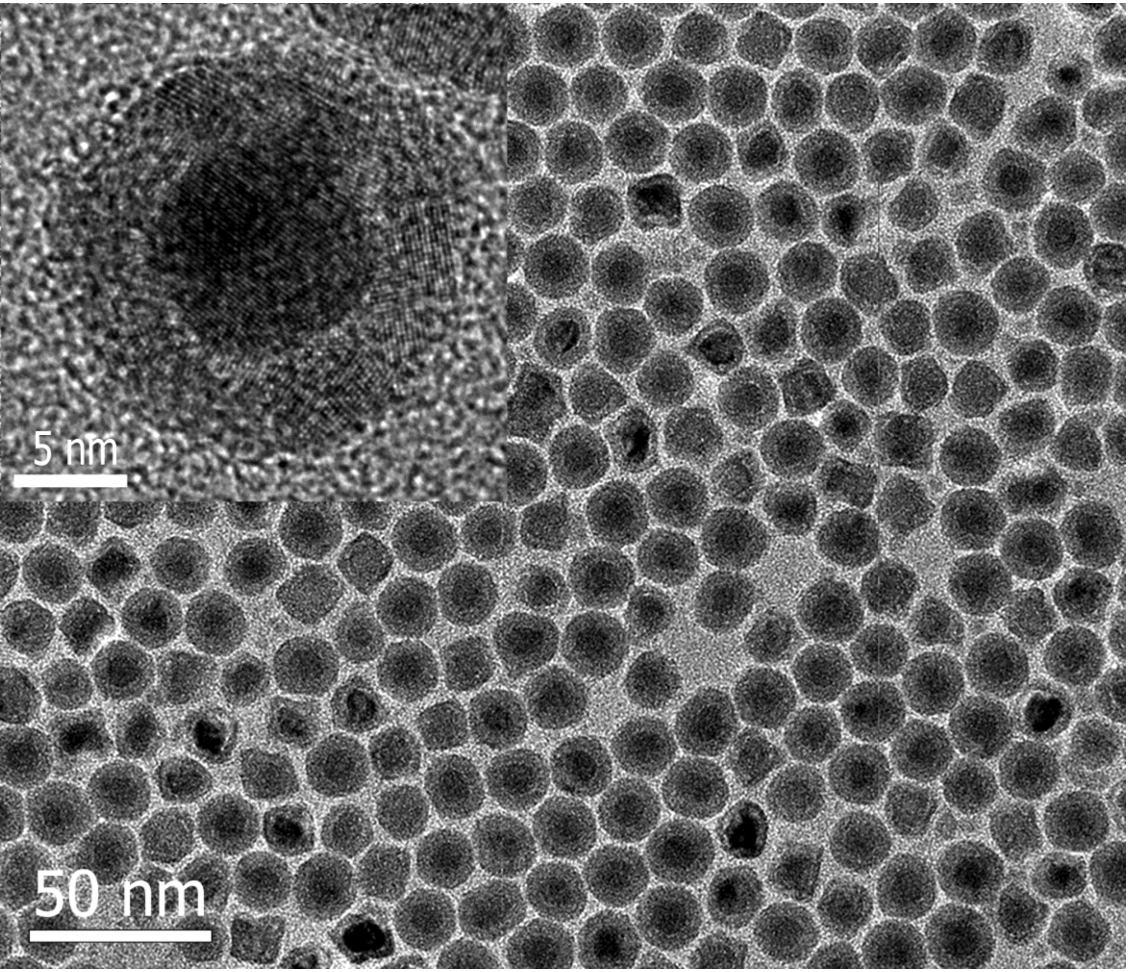




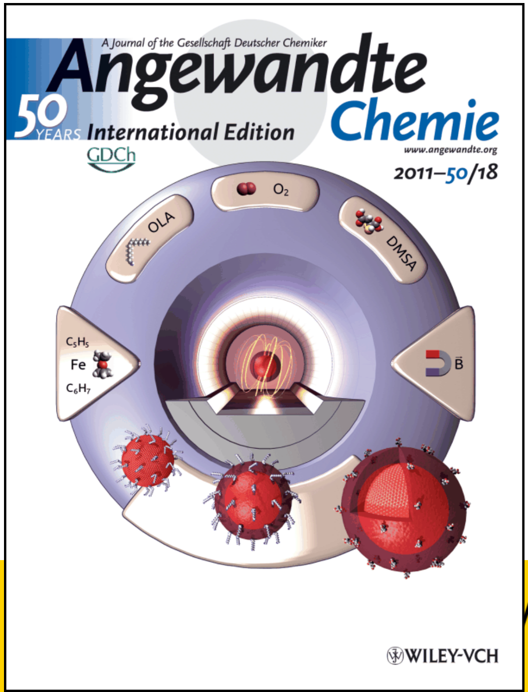
B. F. P. McVey *et al* Manuscript in Preparation

Other materials

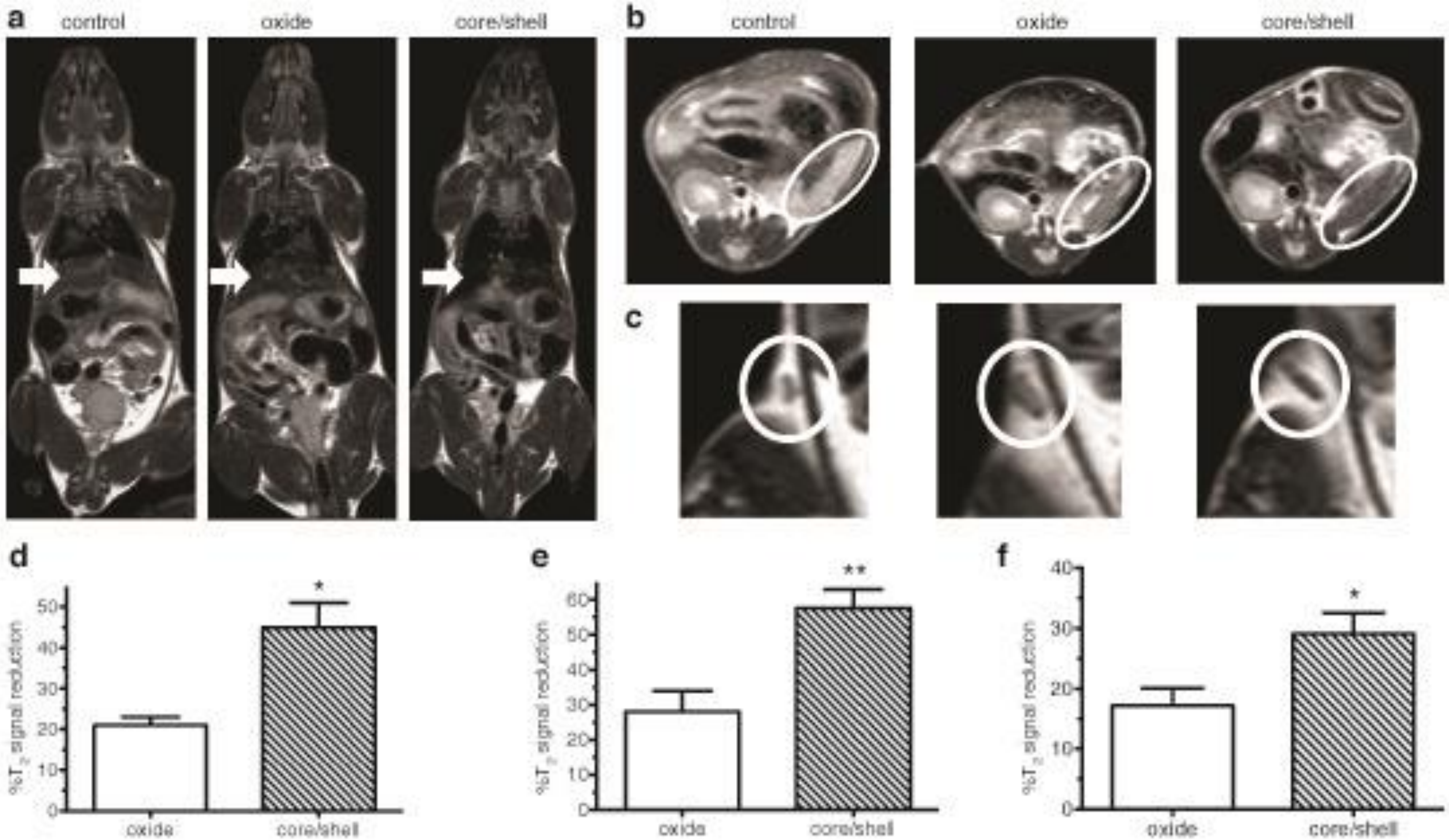
Magnetic Iron particles



- Why iron?
- Low toxicity
- Stronger magnetism.



S. Cheong, P. Ferguson and coworkers, *Angew. Chem. Int. Ed.* 50, 4206–4209 (2011).

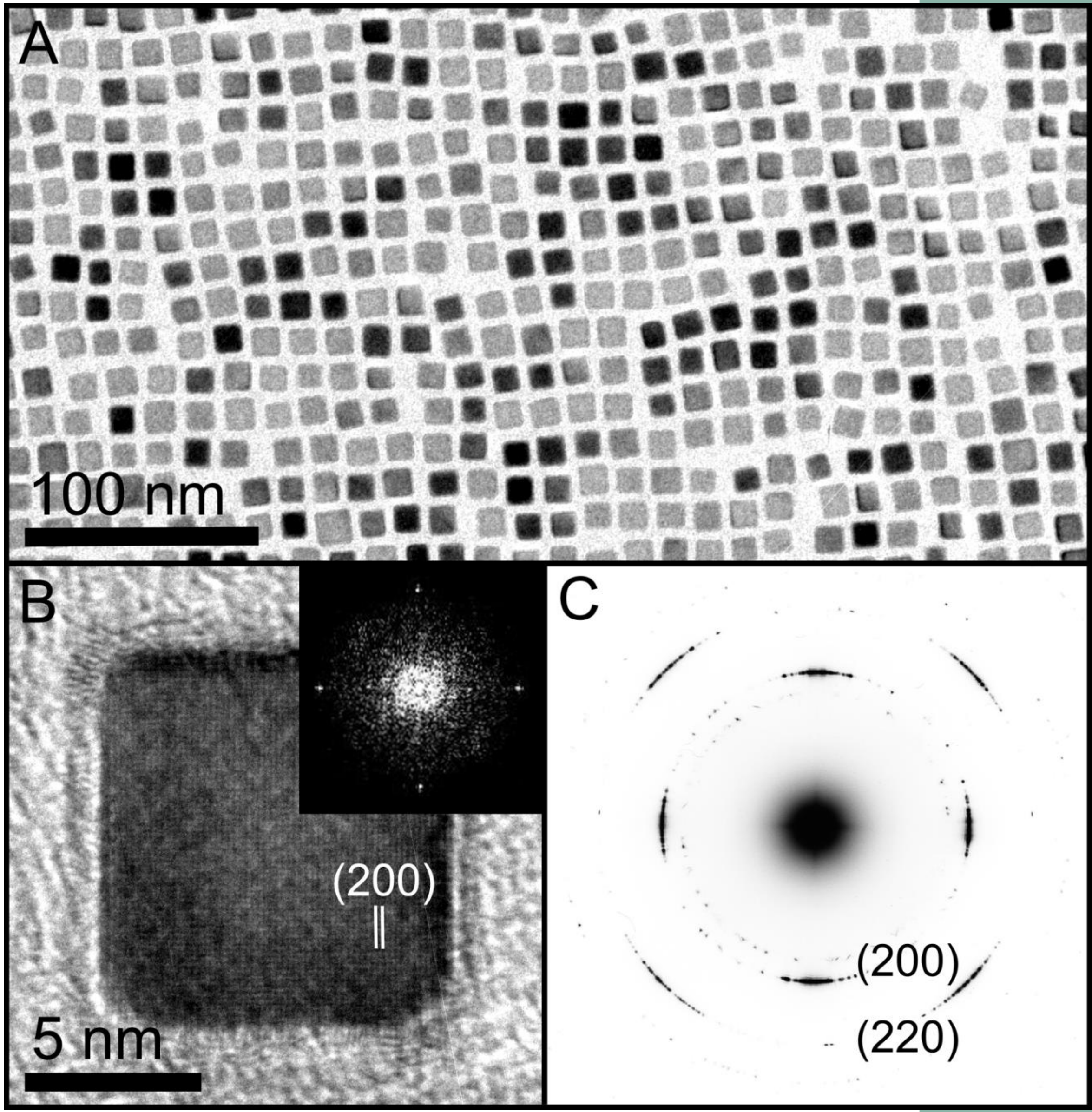


- With Prof. Chen-Sheng Yeh (NCKU, Taiwan)
- Contrast twice of iron oxide control r_2 of 324 $mM^{-1}\ s^{-1}$
- Contrast in liver 1/3 of clinical dose. 2mm tumours.
- Scale up

S. Cheong, P. Ferguson and others, *Angew. Chem. Int. Ed.* 2011, **50,** 4206–4209.

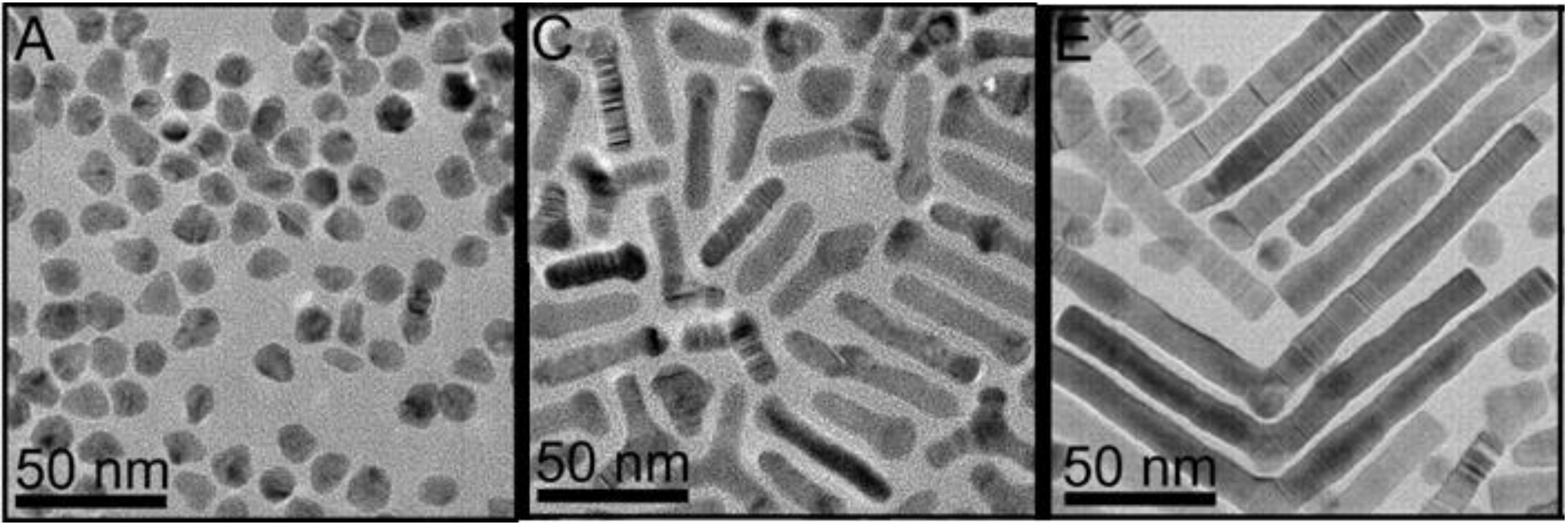
Ni cubes

- Trioctylphosphine + 1 bar H_2
- Stabilizes {100} faces



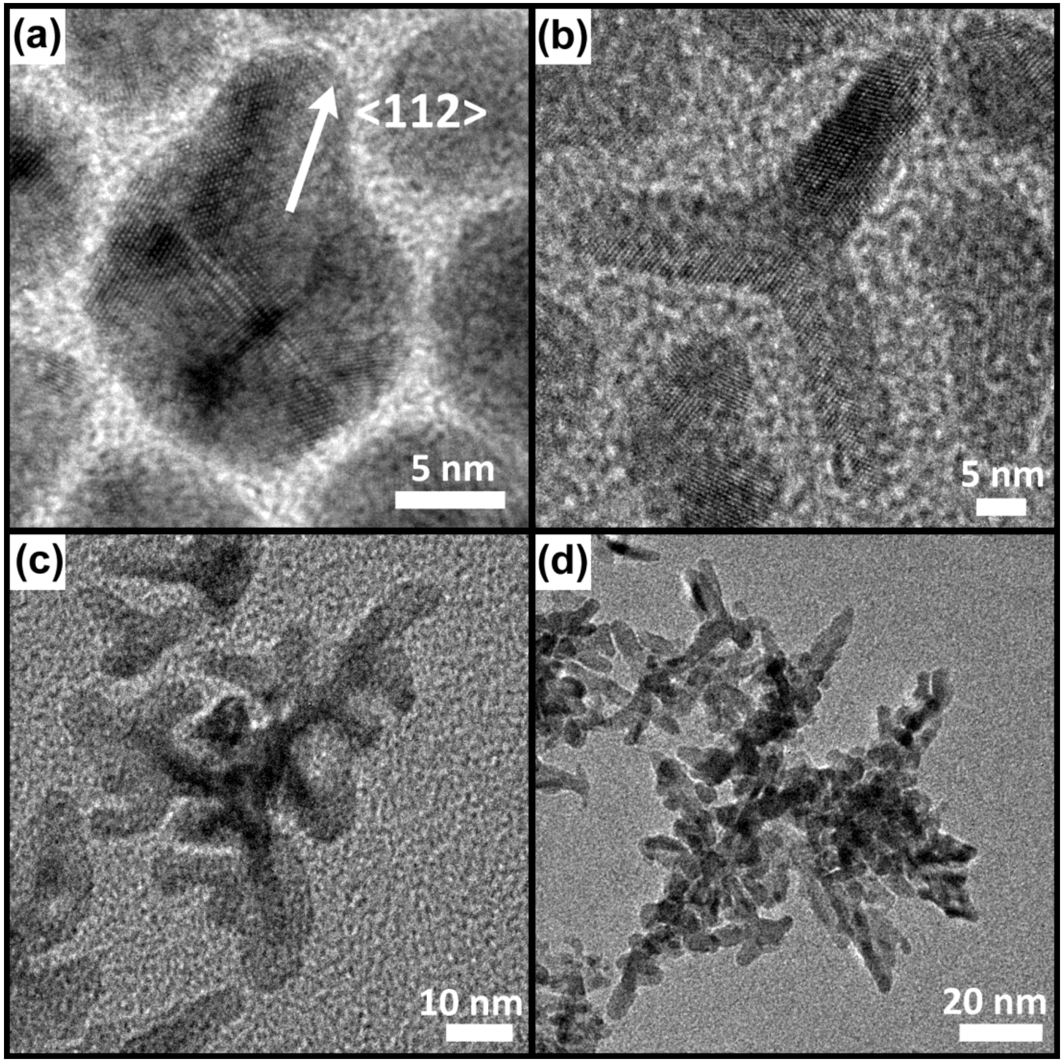
A. P. LaGrow, and coworkers *JACS*, 134, 855-858 (2012).

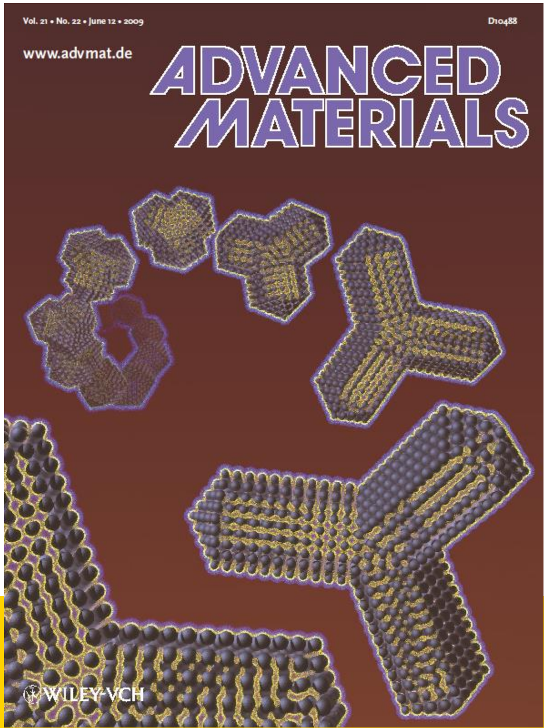
Shape control of Ni



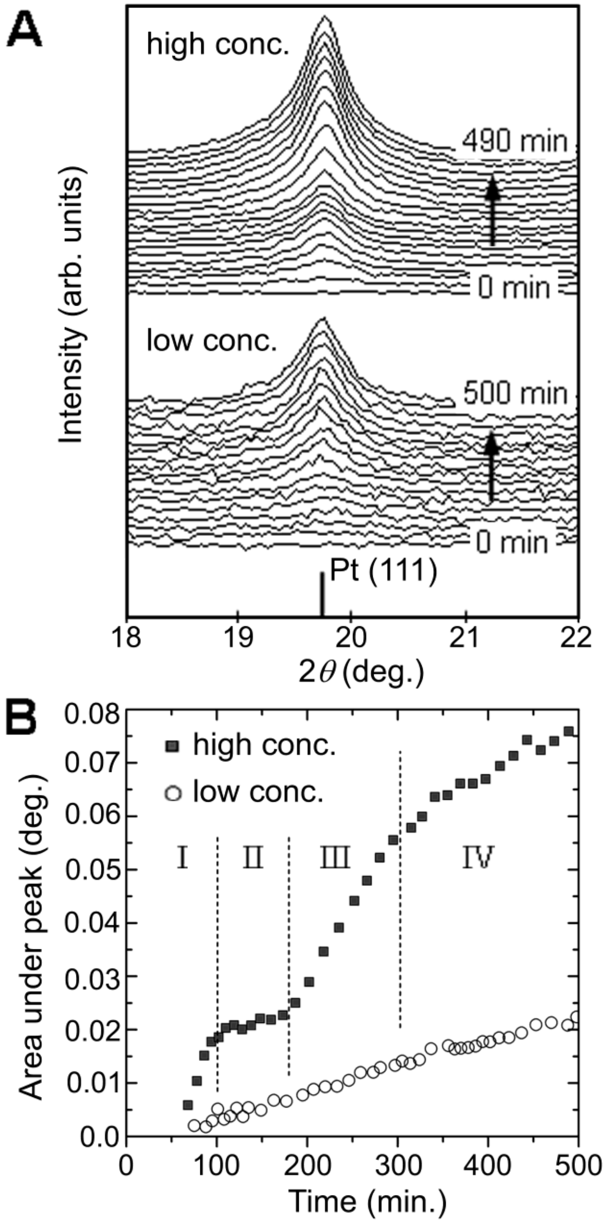
A. P. LaGrow, and coworkers *Advanced Materials*, 25, 1552-1556, (2013).

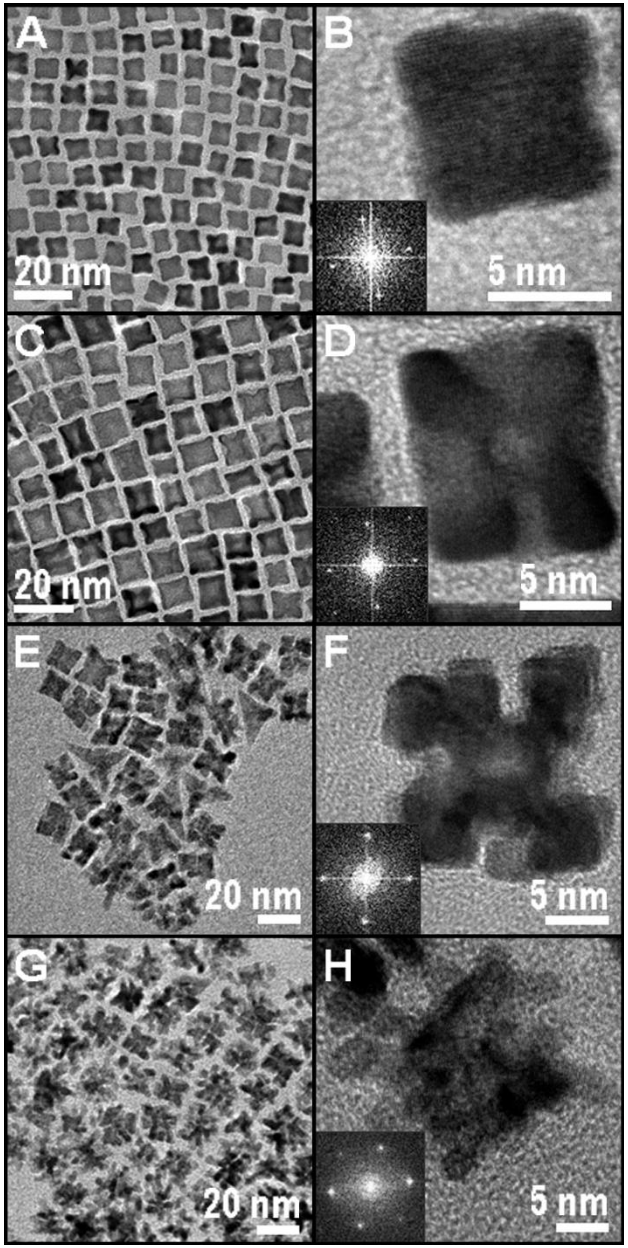
Pd nanocrystals - Growth Mechanism





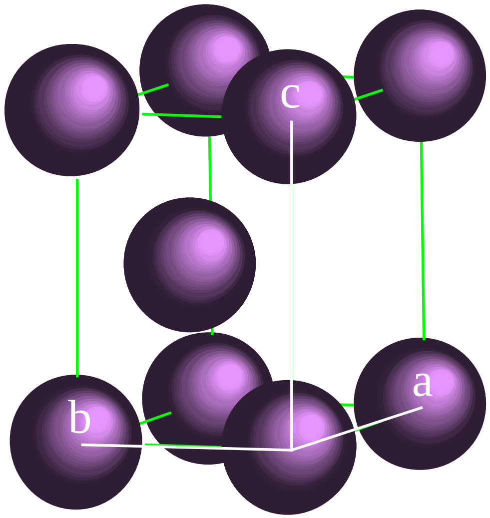
J. Watt *et. al*. *Adv. Mater.*, 21, 2288 (2009).



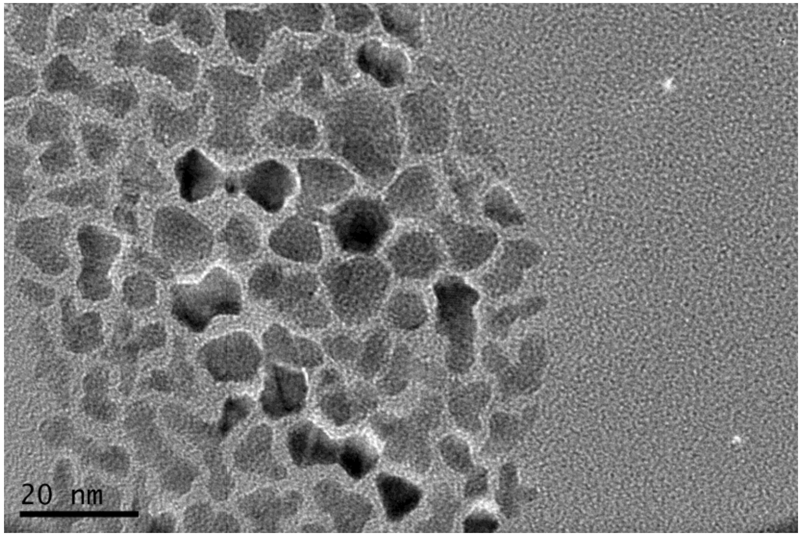


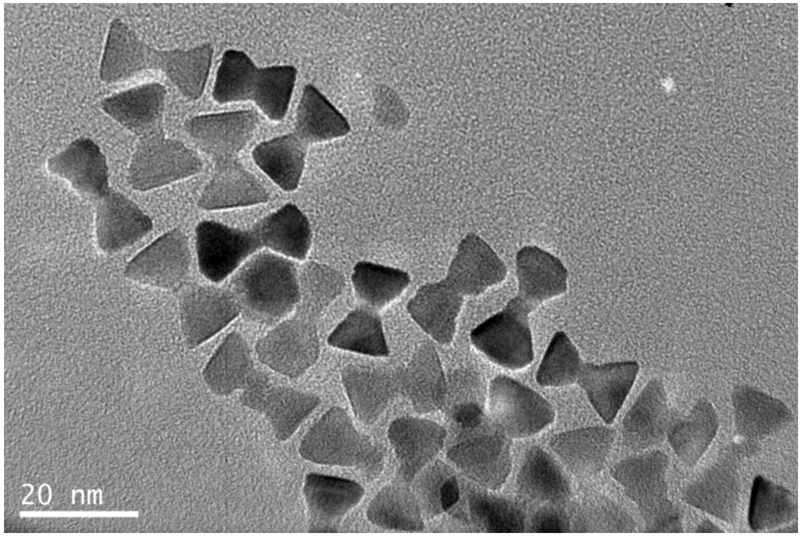
S. Cheong *et. al* JACS, 131, 14590 (2009).

Ruthenium



- Substitute oleylamine with dodecylamine
- Hourglass shape
- Predictive?!

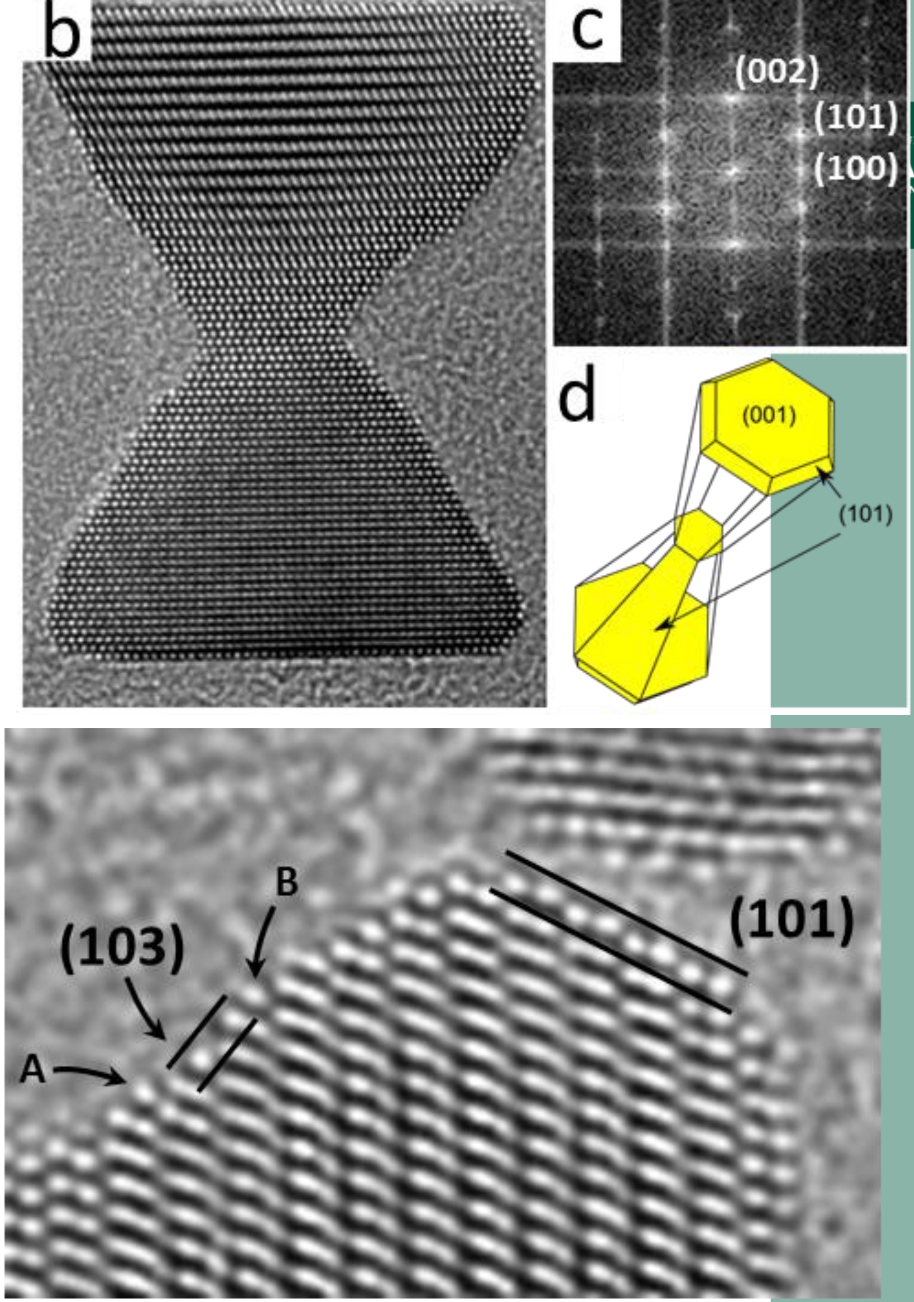




Ruthenium

- Straight chain amine
- Packs better on surface

- Dr Shery Chang (monash)



John Watt, Chenlong Yu.... *JACS*, 135, 606-609,(2013).

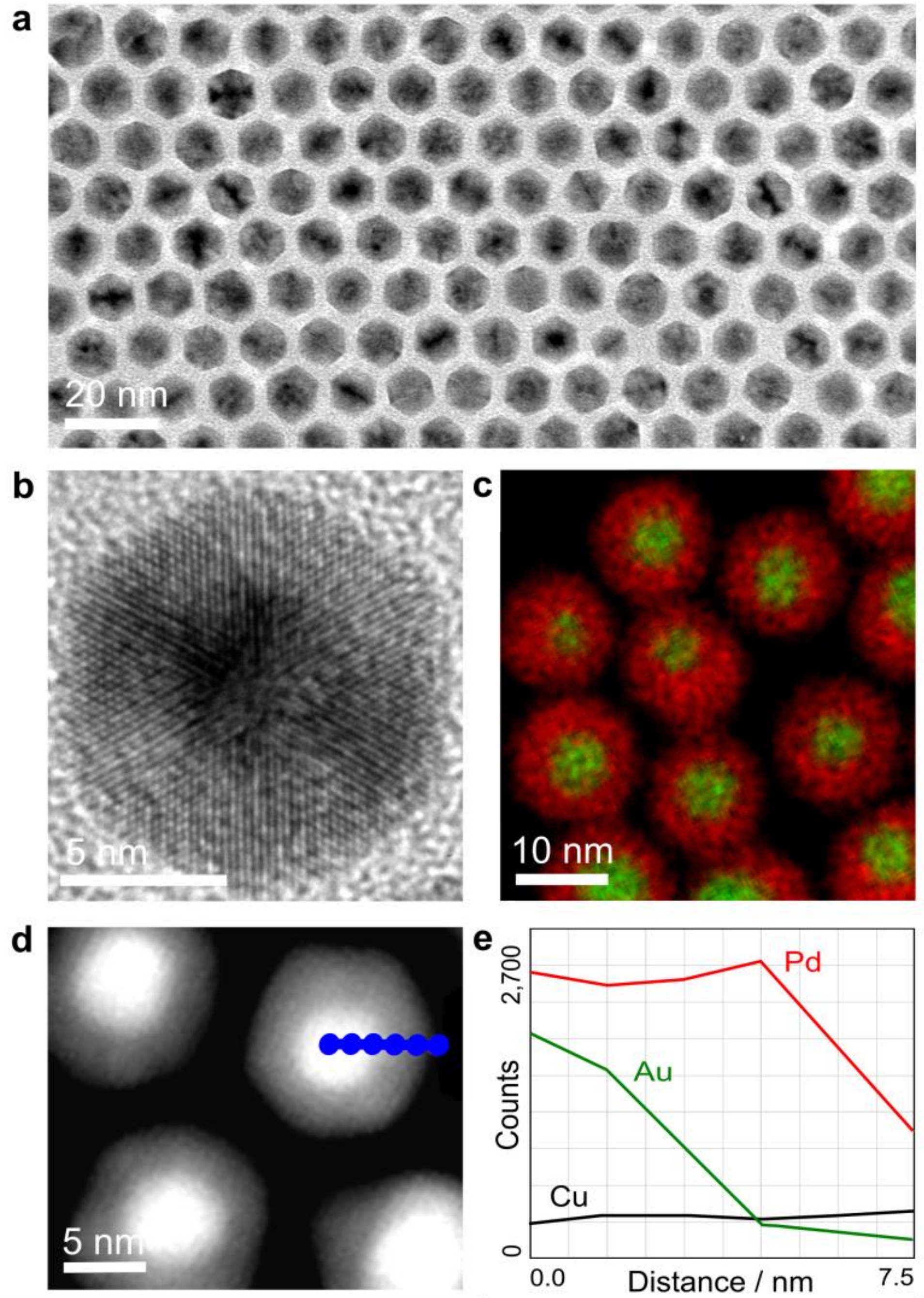
- Au core – Pd shell

- Same size sub 15 nm
- Same shape
- Same composition

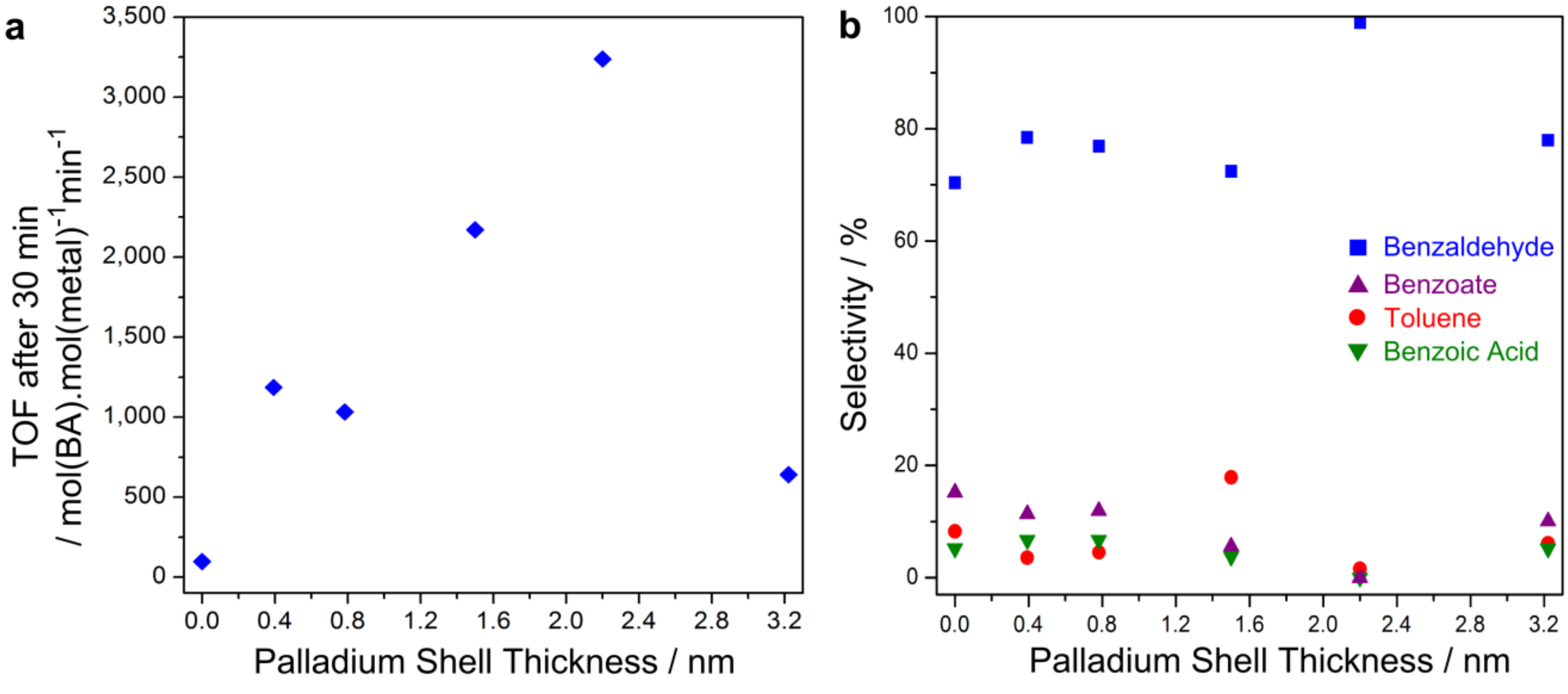
- EDS/EDAX mapping
- HAADF

Prof Angus Kirkland

Dr Yoshihiko Takeda



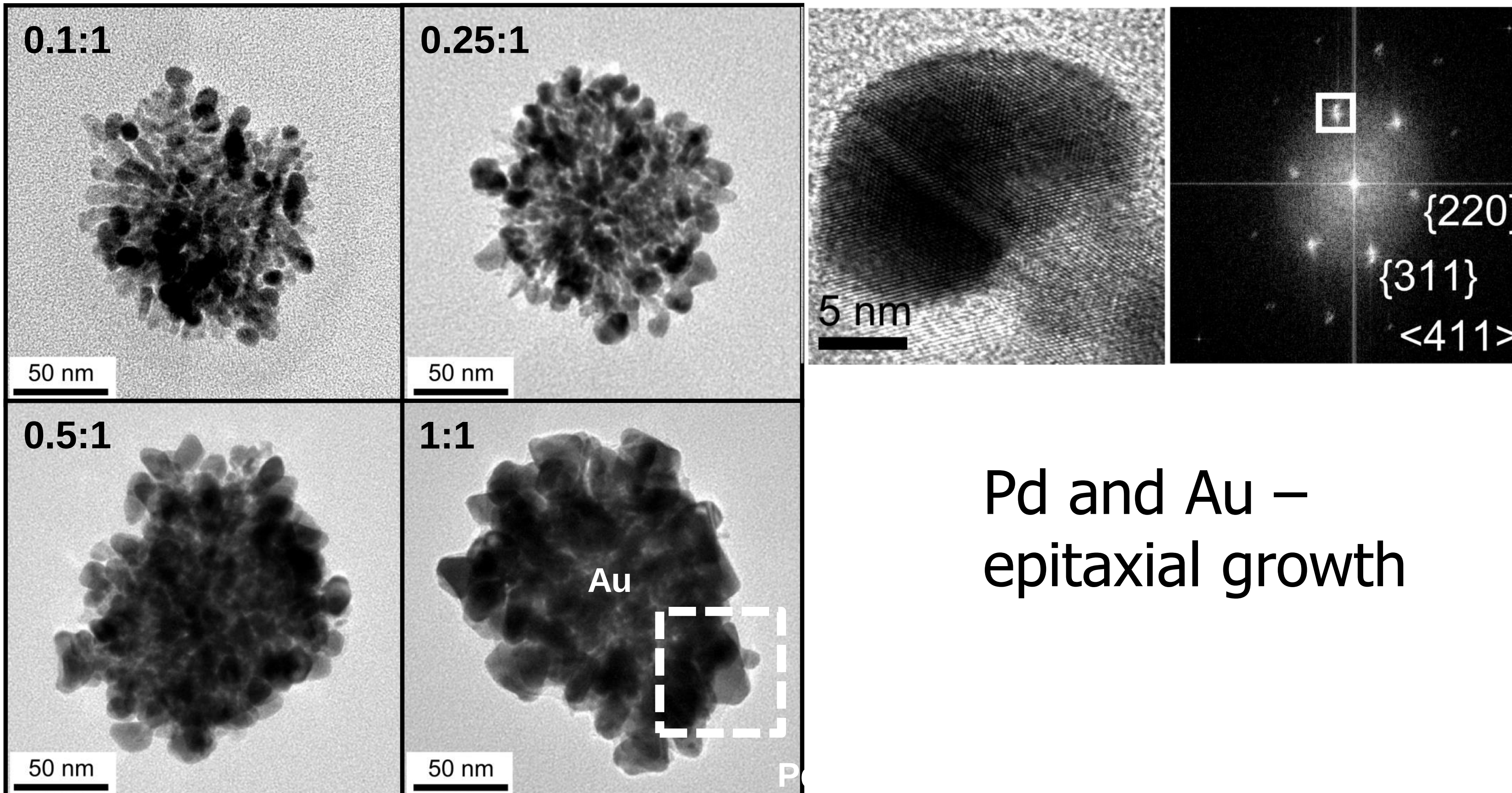
A. Henning and coworkers *Angew. Chem. Int. Ed.* , 52, 1477–1480 (2013).



Oxidation of benzyl alcohol to benzaldehye
(Don’t want toluene)
Max activity at 2.2 nm shell (about 10 layers)
95% selectivity
With stuart taylor (cardiff)

A. Henning and coworkers *Angew. Chem. Int. Ed.* , 52, 1477–1480 (2013).

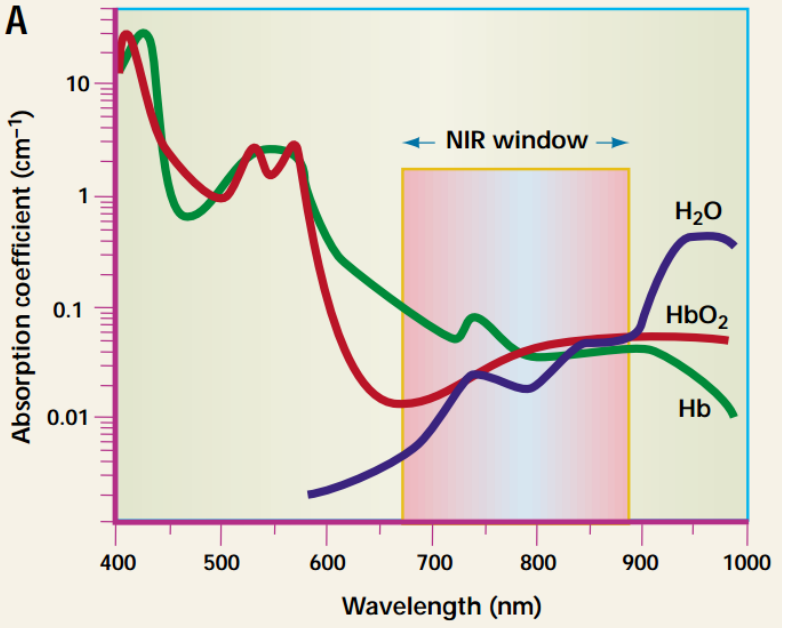
PdAu heterostructures



Pd and Au –
epitaxial growth

A.McGrath and coworkers, submitted

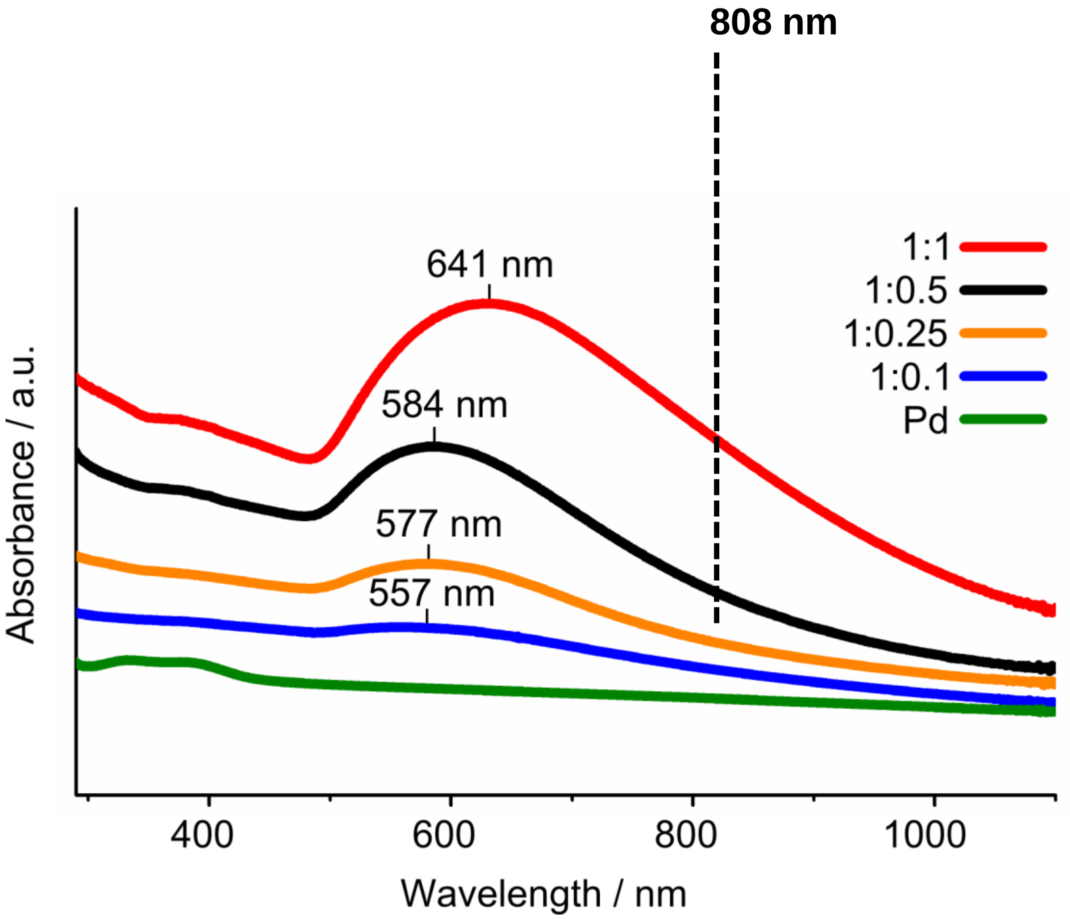
Au on Pd Hyperthermia therapy



- Branched gold structures?
- Local heating of tumour tissue (>45 ºC)
- Laser light transmittable through human tissue in near-infrared (NIR)
- Can be absorbed by nanomaterials, converted to heat

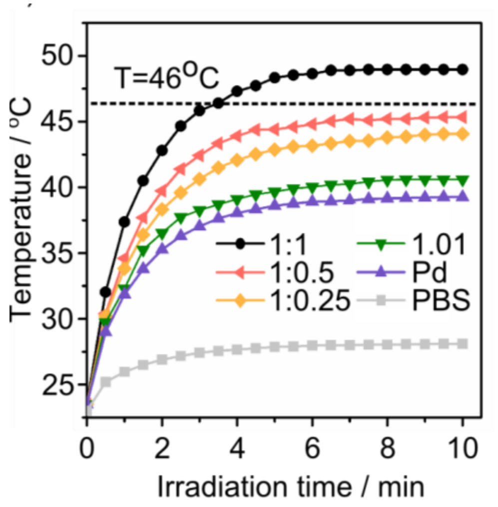
1. R. Weissleder, *Nat. Biotech.*, **2001**, 19, pp 316-317

Near-infrared (NIR) absorbance

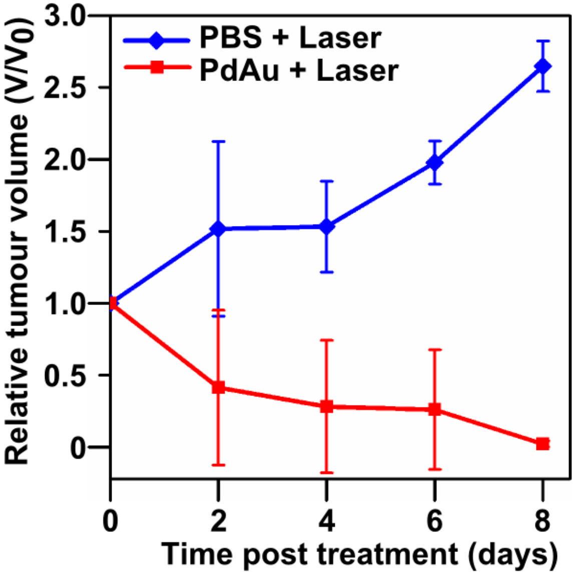


Increasing absorbance at λ = 808 nm with [Au]

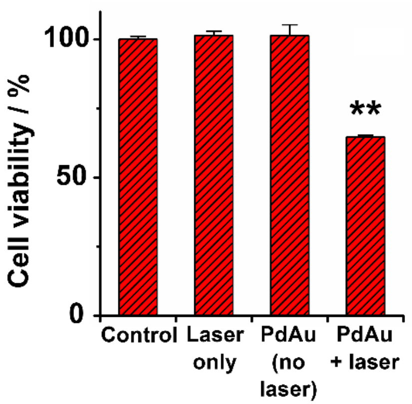
Hyperthermia



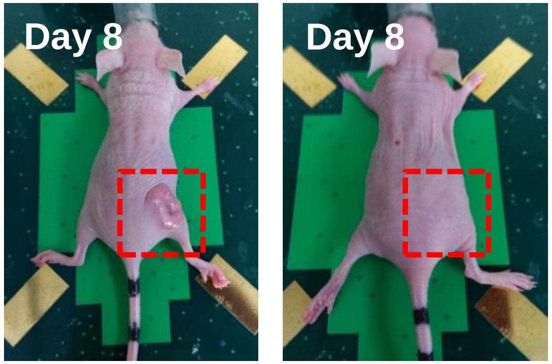
808 nm
laser irradiation



HeLa carcinoma cell cultures



After
5 min
irradiation



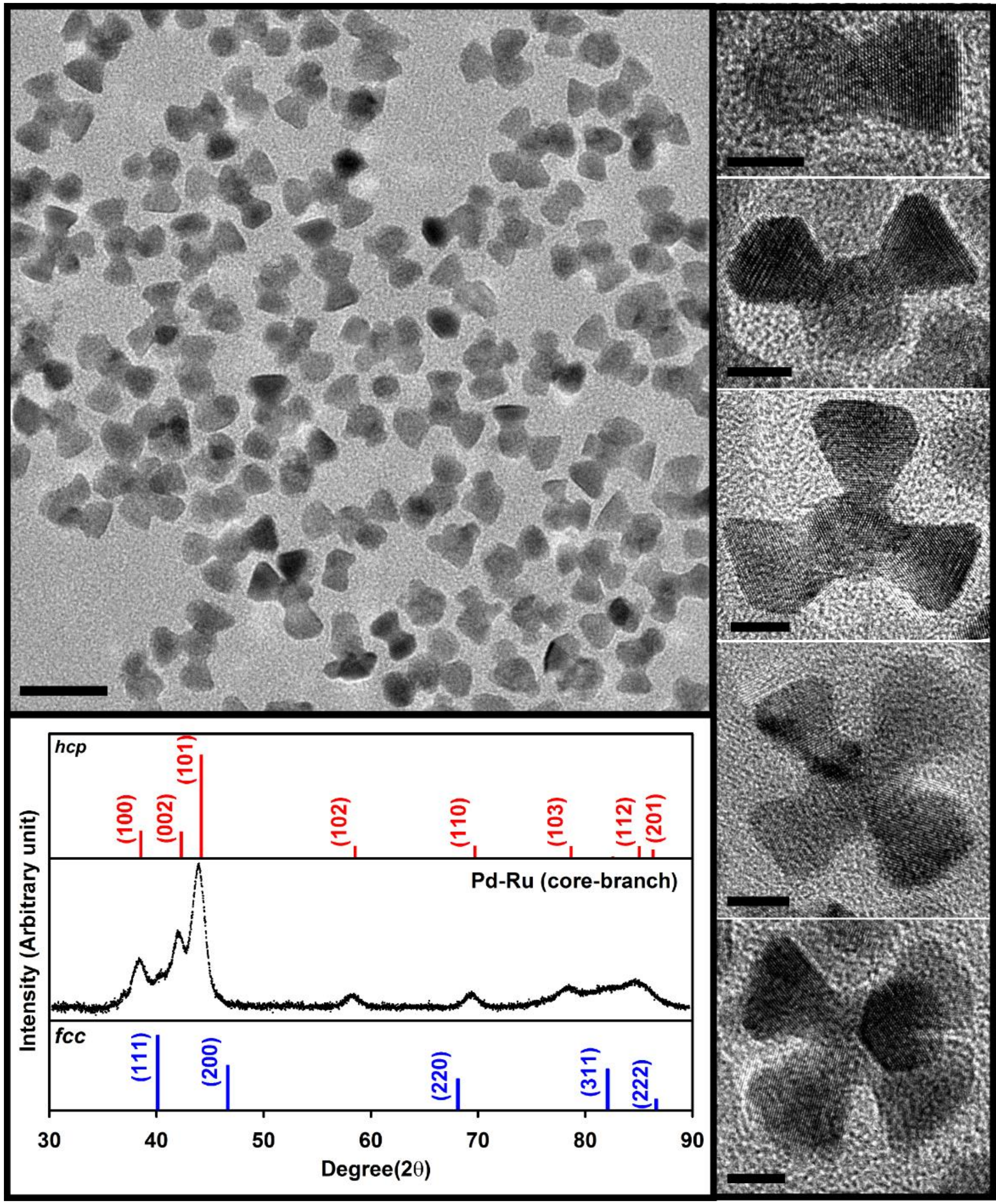
PBS + Laser (3 W cm^{-2}, 30 min)

PdAu + Laser (3 W cm^{-2}, 30 min)

With Prof. Chen-Sheng Yeh and Dr. Yi-Hsin Chien
(National Cheng Kung University, Taiwan)

Bi-metallic

- fcc Pd core hcp Ru arms
- Build 3-D structures

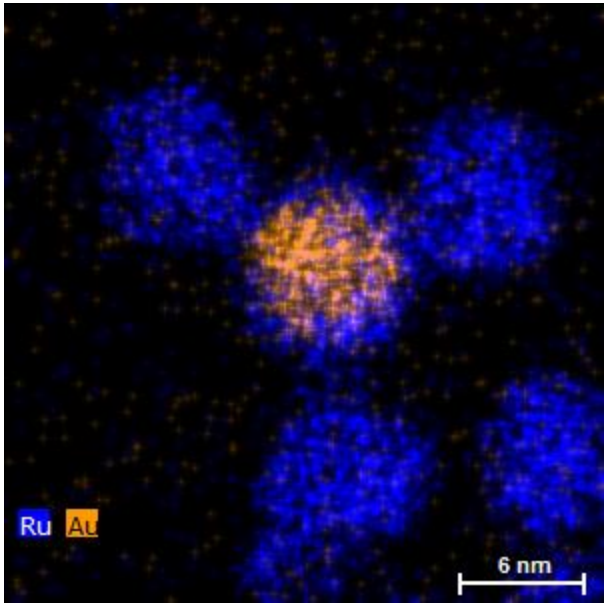


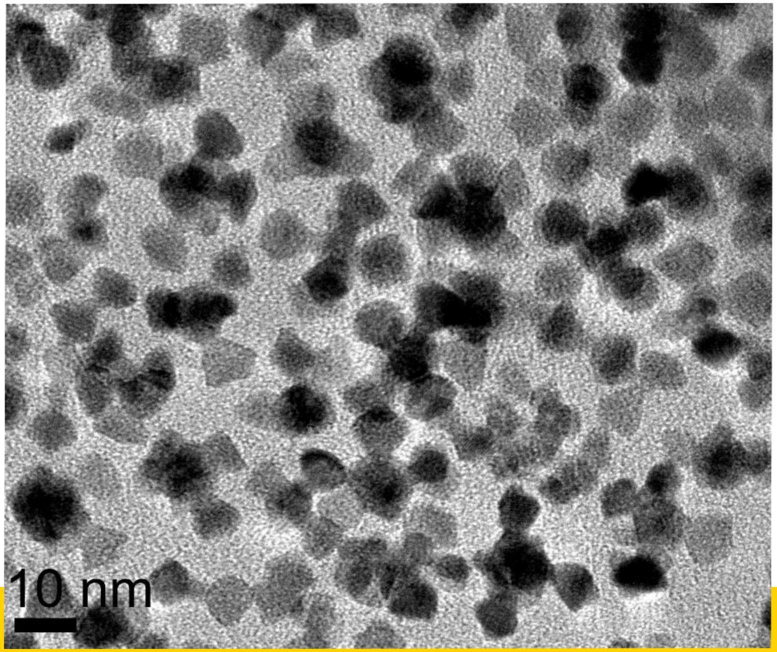
X Chan and coworkers submitted

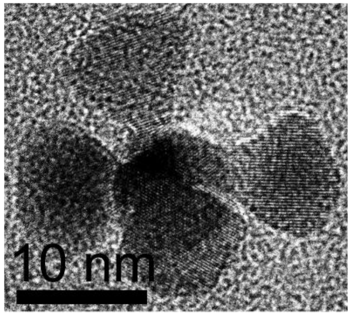
UNSW AUSTRALIA

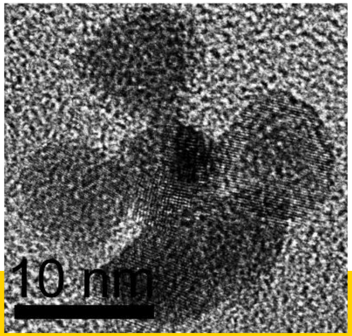
Au core Ru arms

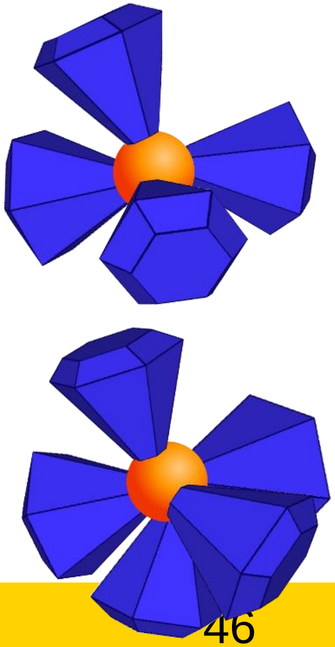
- Au core Ru arms
- Different mechanism
- Amanda Barnard CSIRO











EMU

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Collaborators