Nonthermal plasma synthesis of nanomaterials for energy applications

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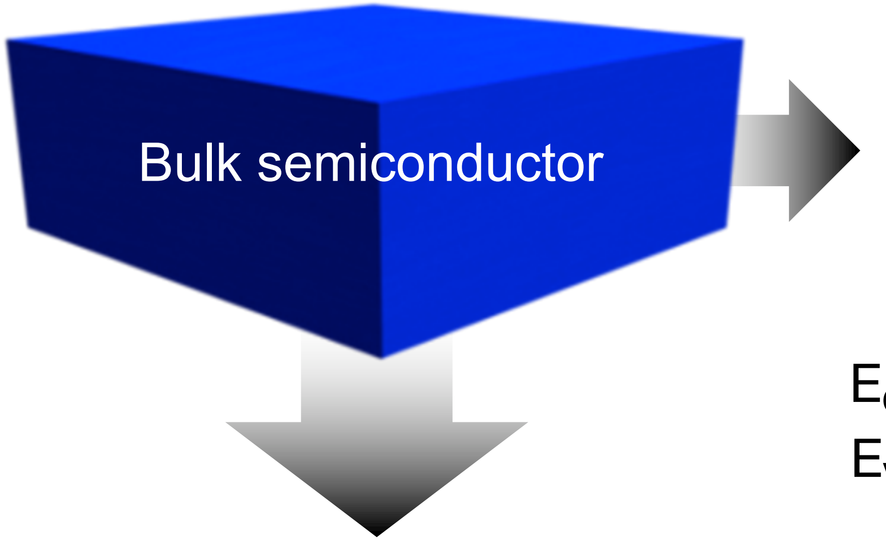
University of Minnesota, Mechanical Engineering

Overview

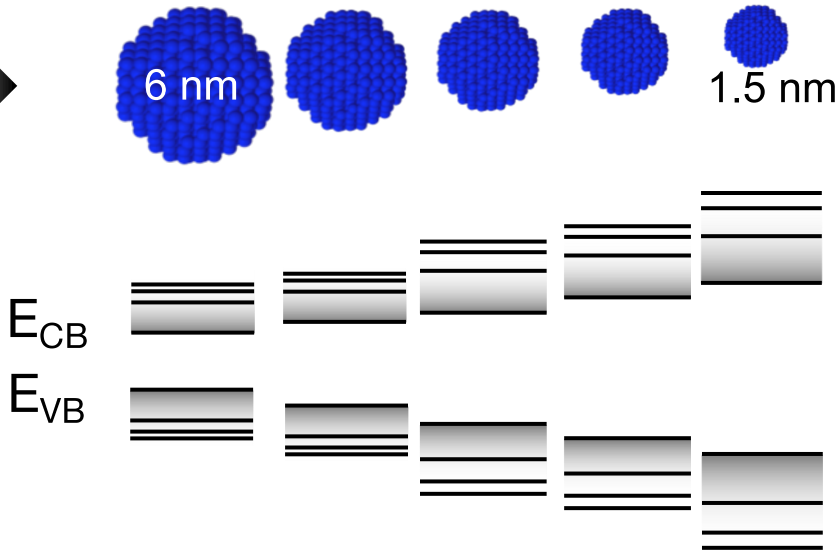
- Introduction: Why nanocrystals?
- Plasma synthesis of nanocrystals
- Silicon luminescent solar concentrators
- Conclusions

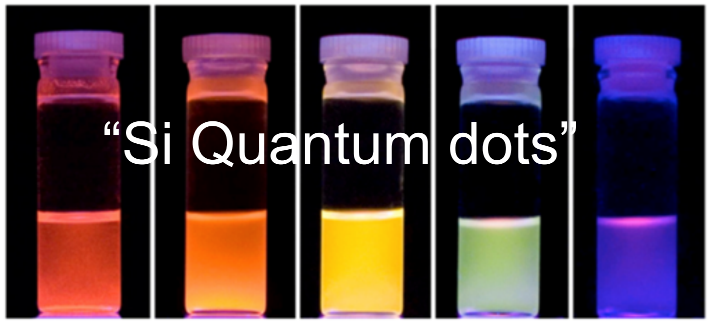
Introduction: Why nanocrystals?

Why Nanocrystals?



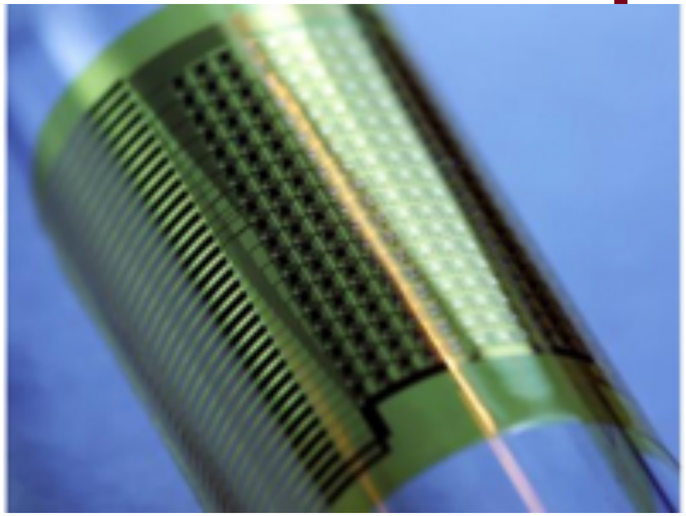
Quantum confinement





Pi, X. D. et al. Nanotechnology (2008).

Vision: printed electronics



http://images.gizmag.com/hero/flexible-electronics.jpg

http://news.cnet.com

Phys.org

http://wikipedia.org

Products on the market

Samsung Quantum dot TV

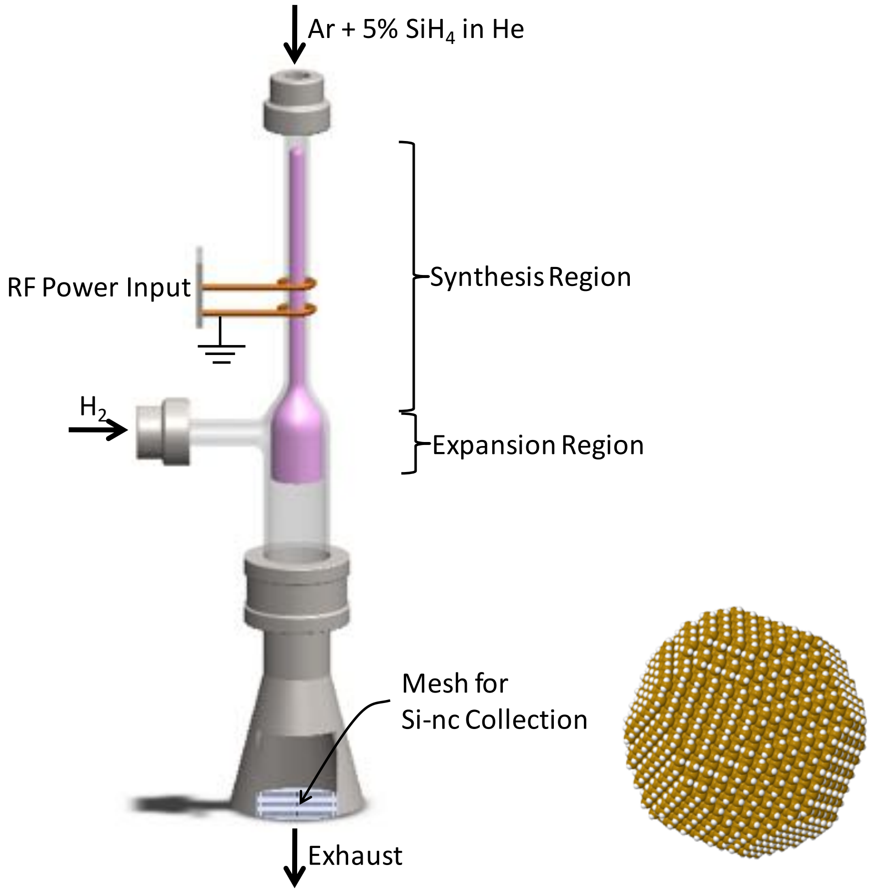
DuPont-Innovalight Si ink

Quantum dot syntheses

Liquid Phase Synthesis

ionically bound NCs (PbX, CdX; X=S, Se, Te)

Gas Phase Synthesis



covalently bound NCs (Si, Ge, nitrides,…)

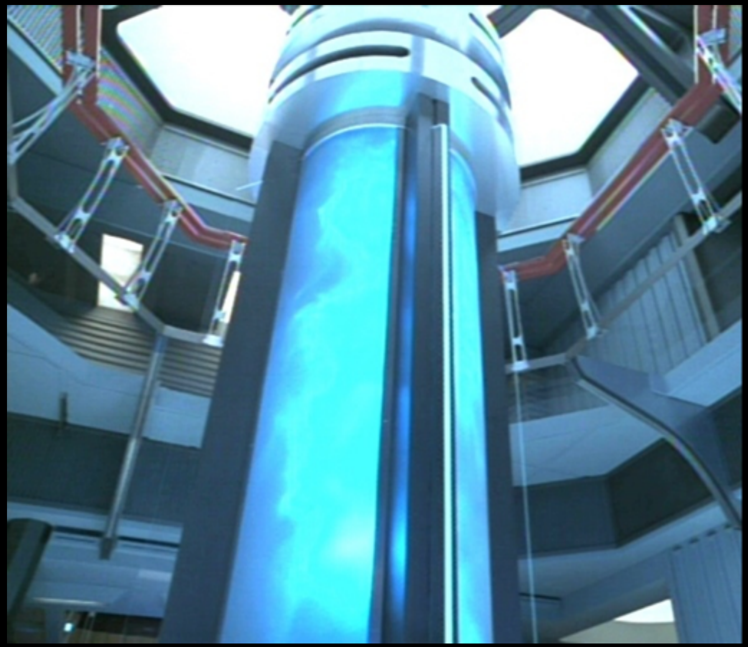
L. Mangolini

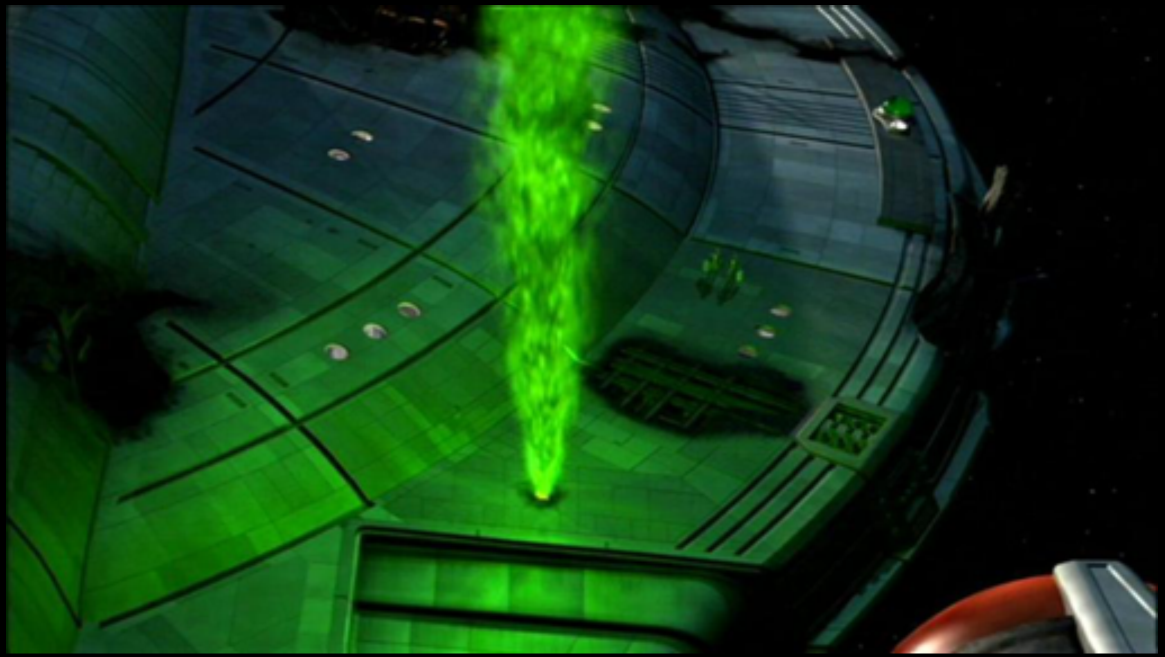
E. Thimsen

Plasma synthesis of nanocrystals

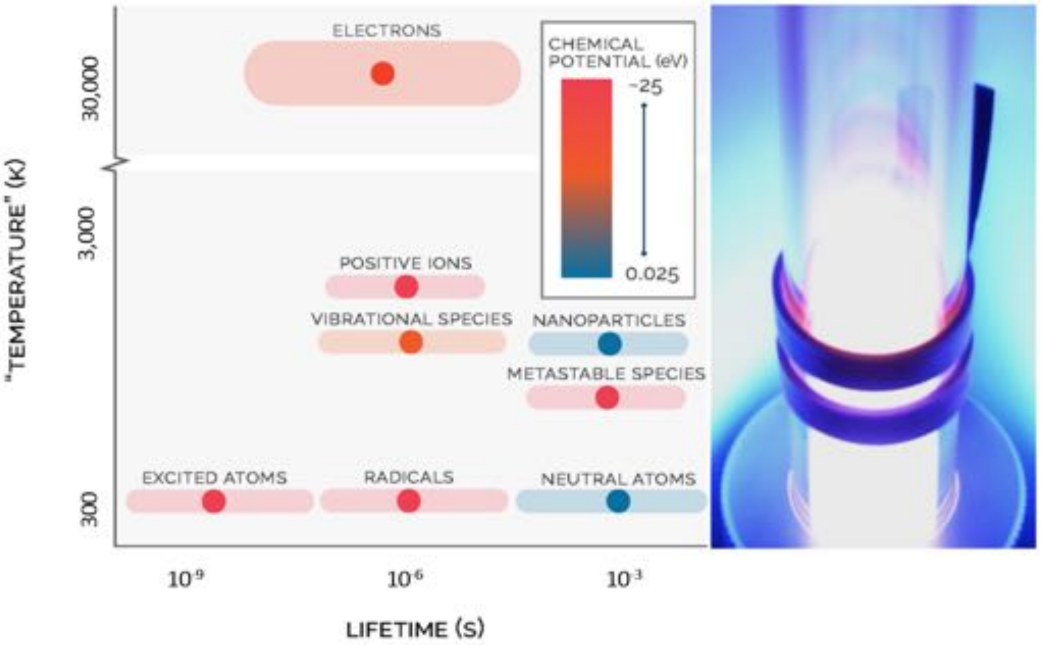
Mangolini, Thimsen, Kortshagen, *Nano Letters*, 2005

Plasmas: Don’t do this at home!

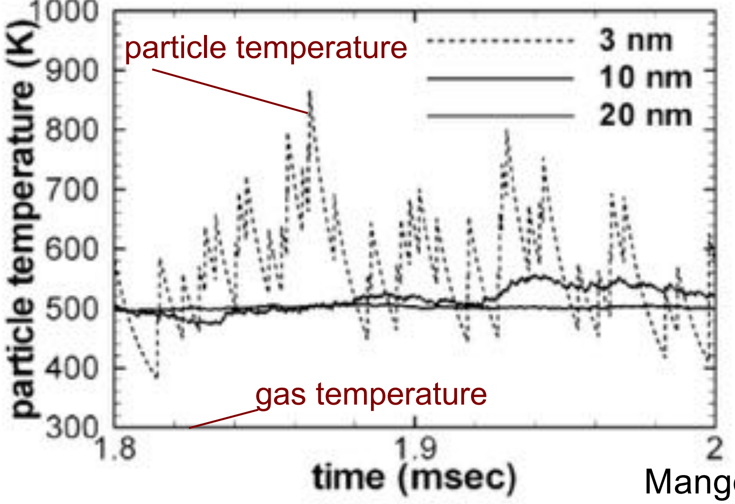


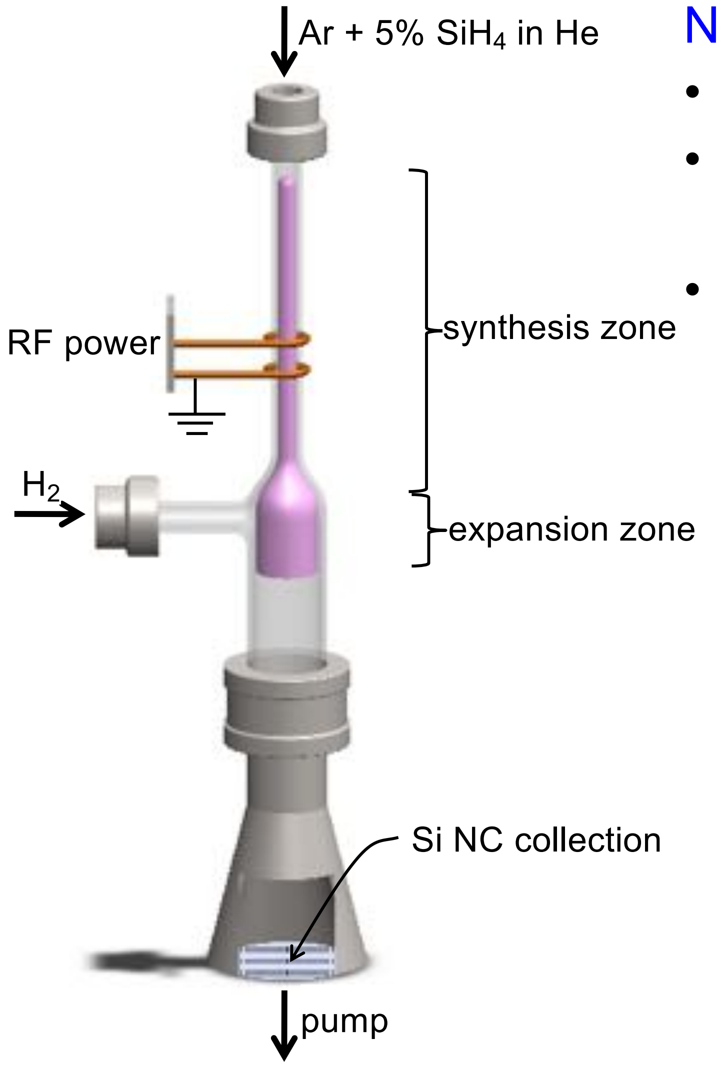


Plasma synthesis: Highly nonequilibrium environment



Monte Carlo simulation

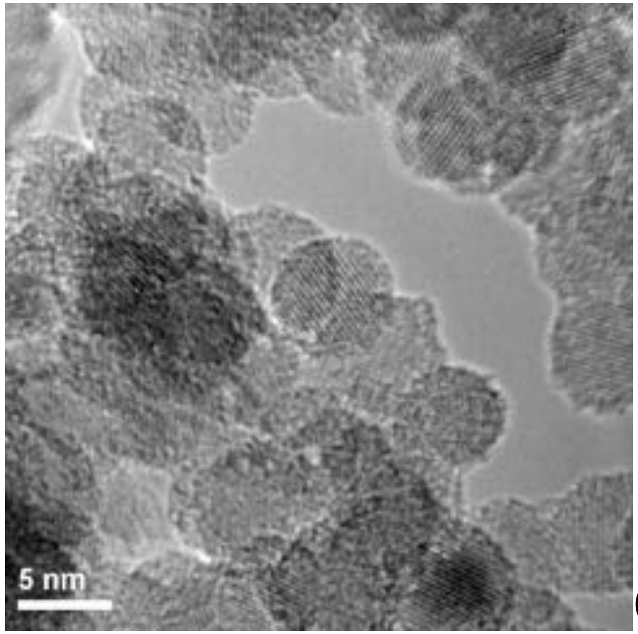




Mangolini, Thimsen, Kortshagen, *Nano Letters*, 2005

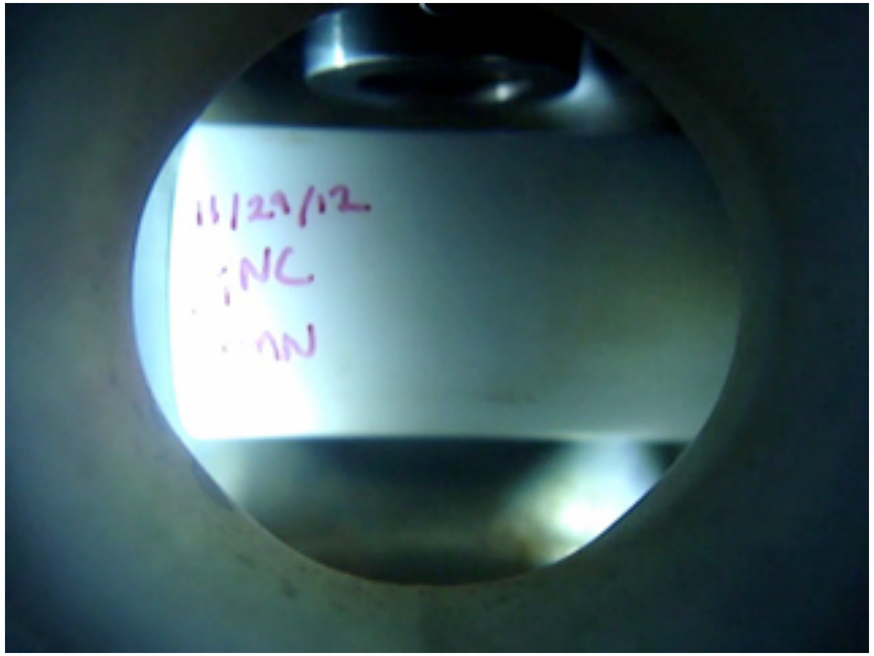
Nonthermal plasma:

- Nonequilibrium environment
- Selective particle heating through surface reactions
- Elimination of agglomeration by unipolar particle charging



Plasma synthesis of nanomaterials

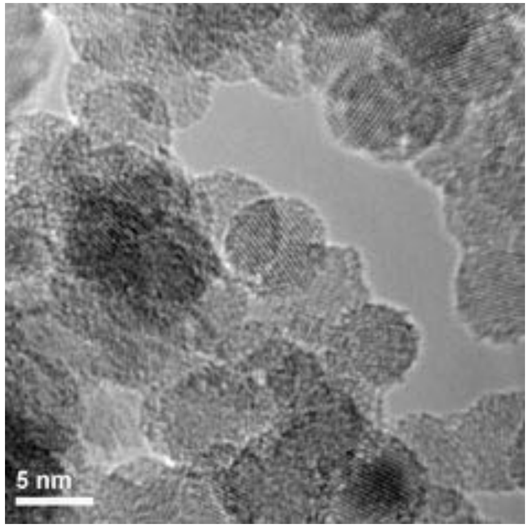
L. Mangolini, E. Thimsen and U. Kortshagen,
Nano Letters **5(4)**, 655 (2005)



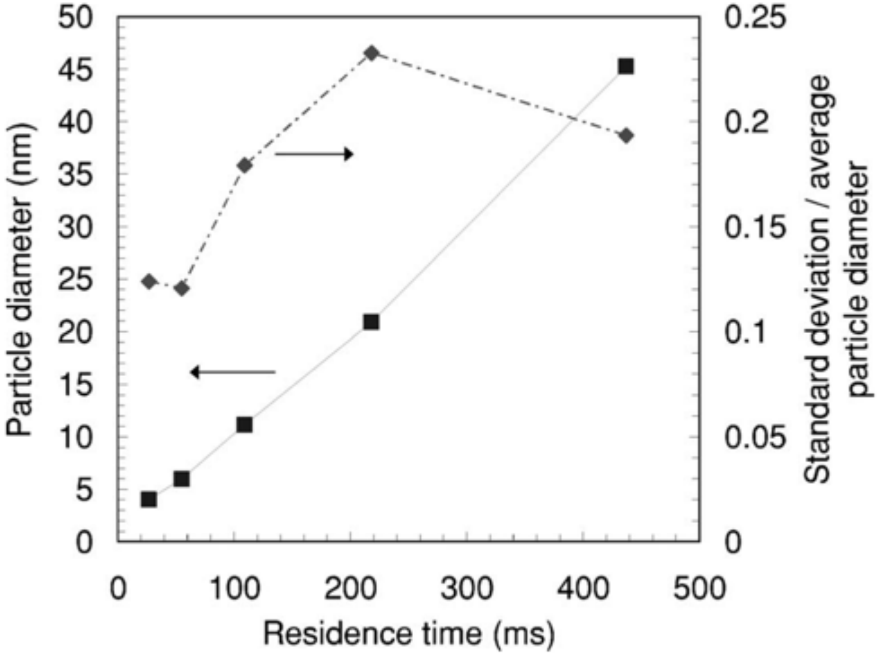
Z. Holman and U. Kortshagen,
Nanotechnology **21(33)** 335302 (2010)

Z. Holman

Plasmas synthesis of group IV nanocrystals



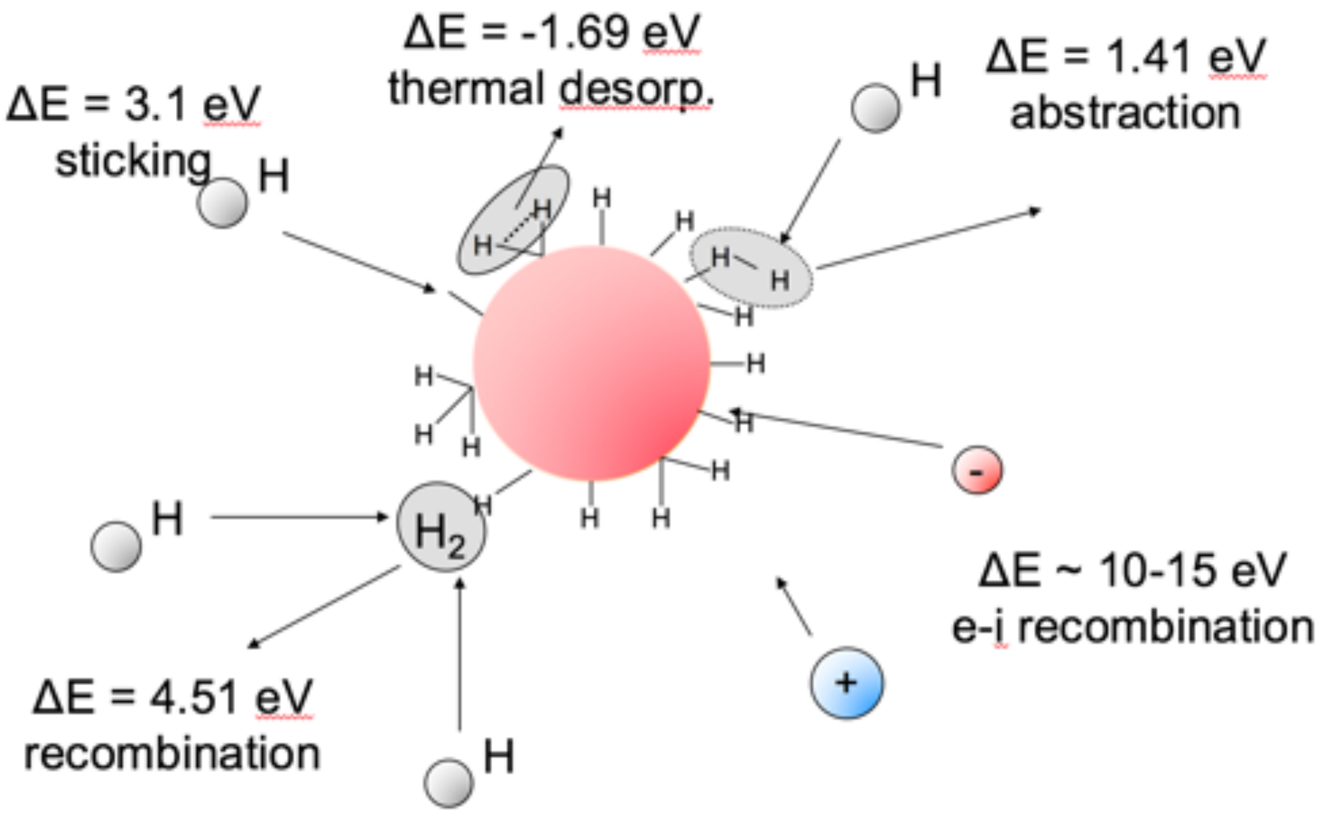
L. Mangolini et al., Nano Letters (2005)



R. Gresback, Z. Holman, U. Kortshagen, Appl. Phys. Lett. **91**, 093119 (2007) (for Ge NCs from $GeCl_4$)

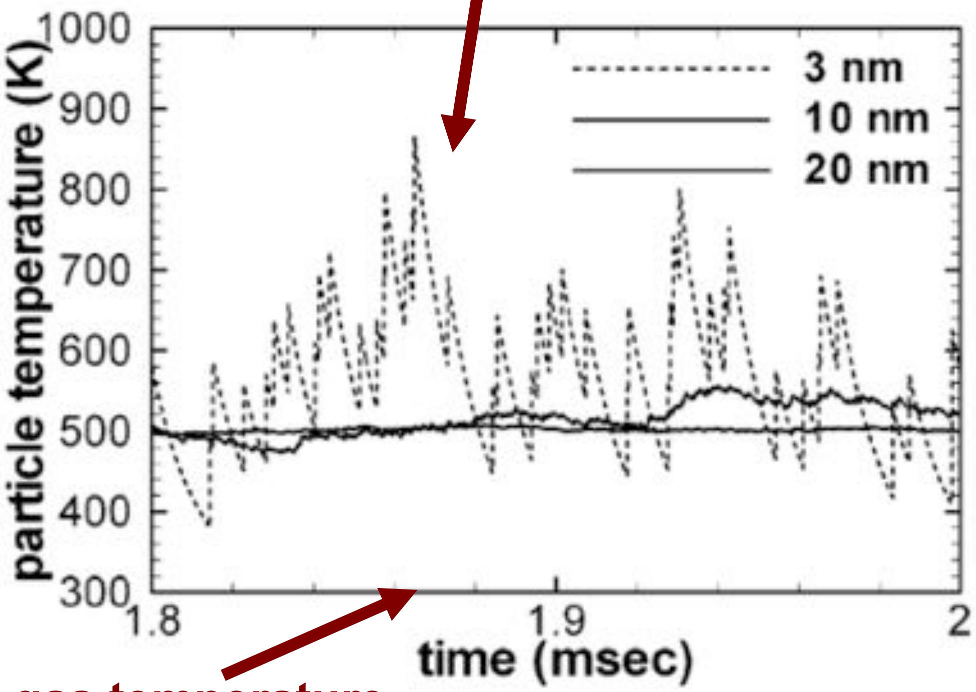
- materials that require high temperature
- particle size control through residence time
- relatively good monodispersity

Heating of NCs in plasmas

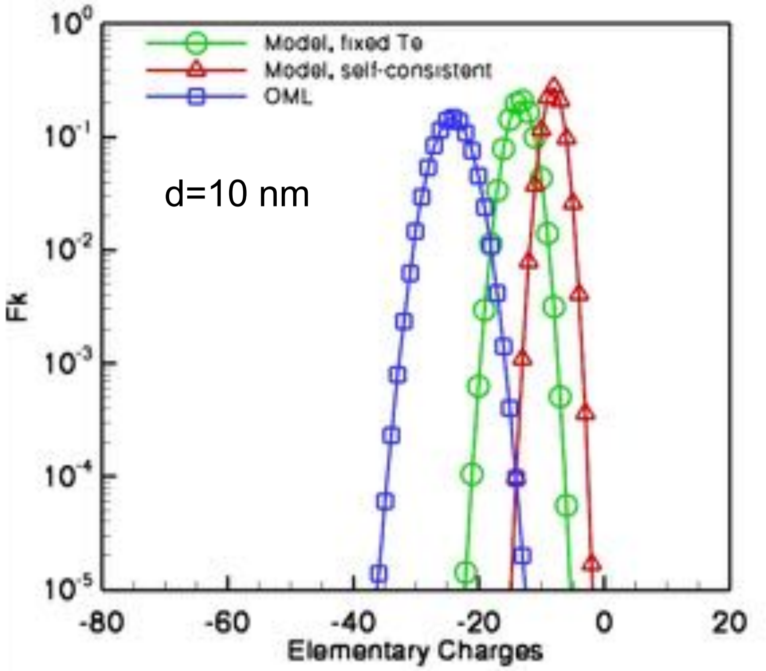


Characteristics NCs in Plasmas

particle temperature



gas temperature

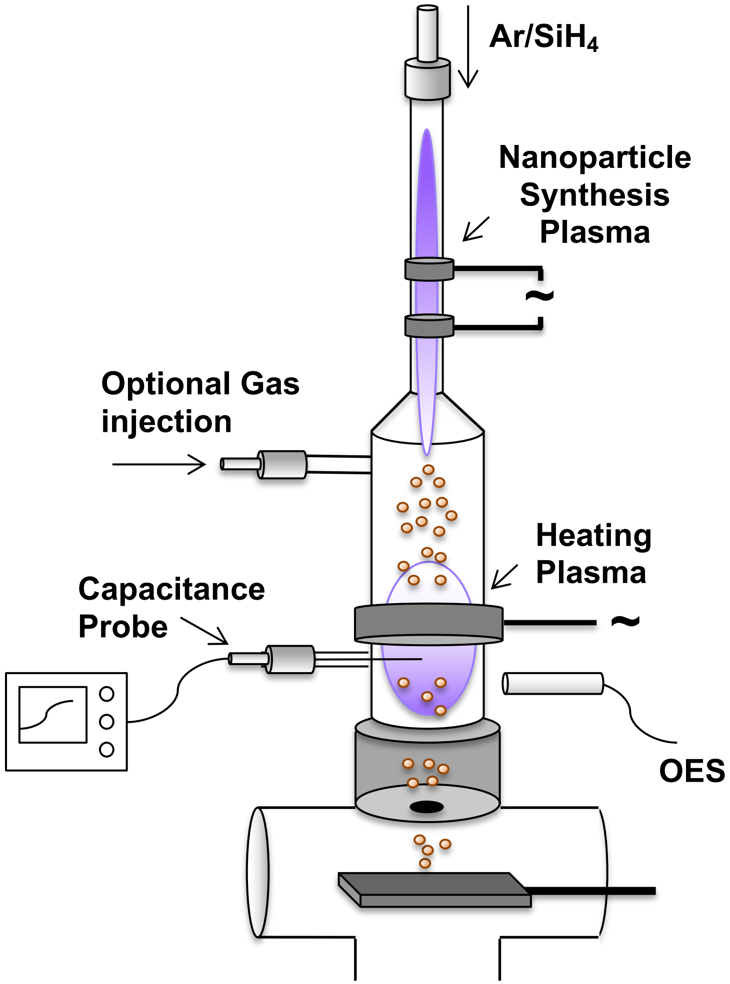


L. Mangolini et al., Nano Letters (2005)

F. Galli, U. Kortshagen,
IEEE Trans. Plasma Sci. (2010)

Experimental Study of NP Heating

- Decoupling of nanoparticle synthesis and heating.
- Amorphous silicon nanoparticles in a low power primary plasma.
- Heat the nanoparticles in a variable power secondary plasma.
- Study conditions necessary to crystallize the nanoparticles in the second plasma.

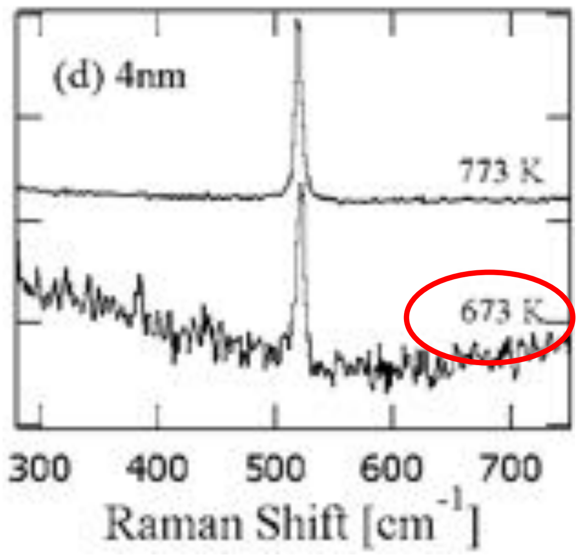


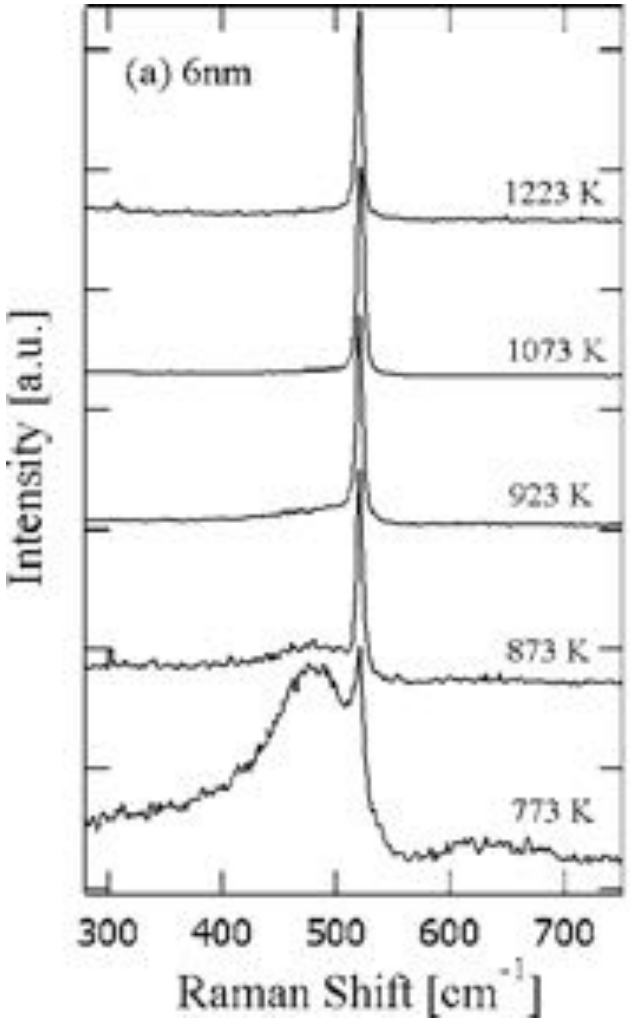
Nic Kramer

Rebecca Anthony

N. Kramer et al., J. Phys. D: Appl. Phys. **47** (2014) 075202

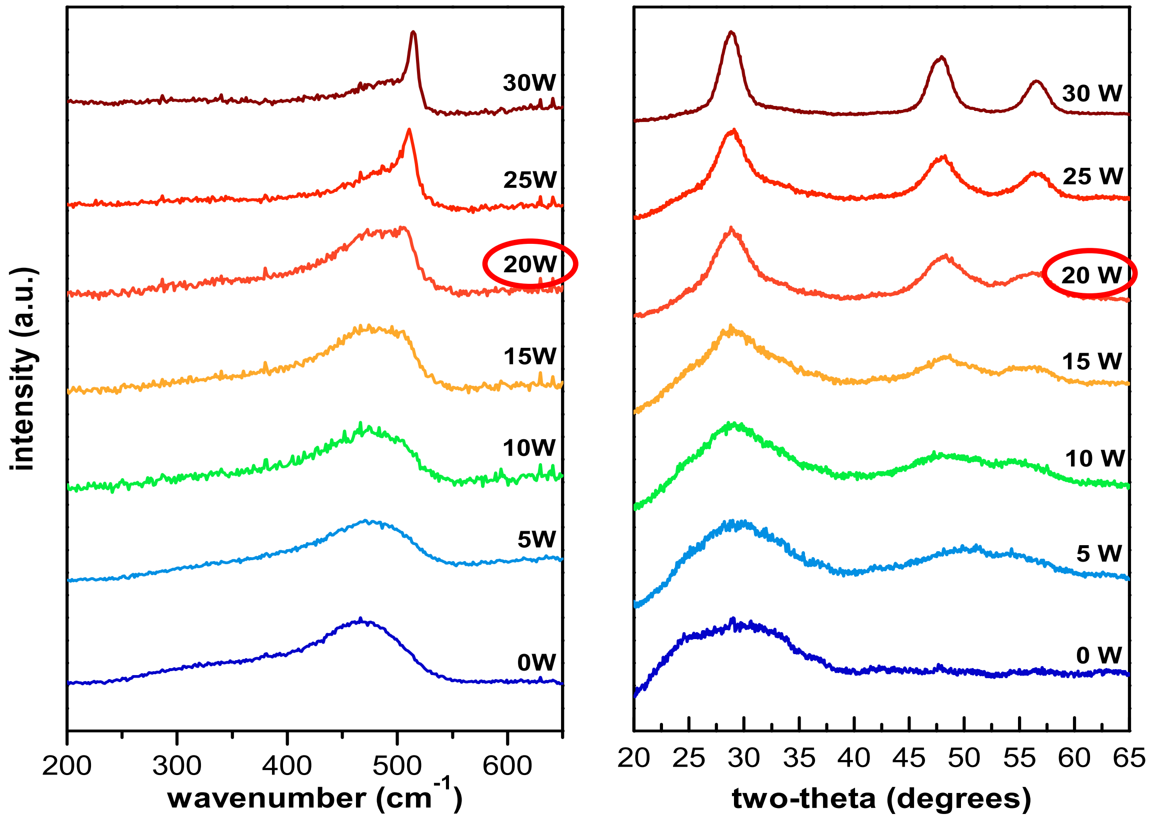
Nanoparticles as Thermometers

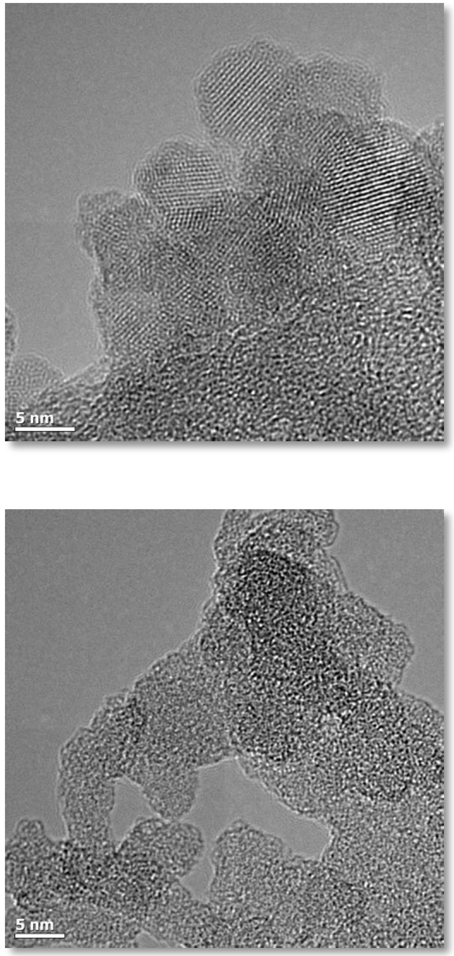




Hirasawa, M., Orii, T., Seto, T., *Appl. Phys. Lett.*, 88, 093119, **2006**

Nanoparticle Raman, XRD, TEM



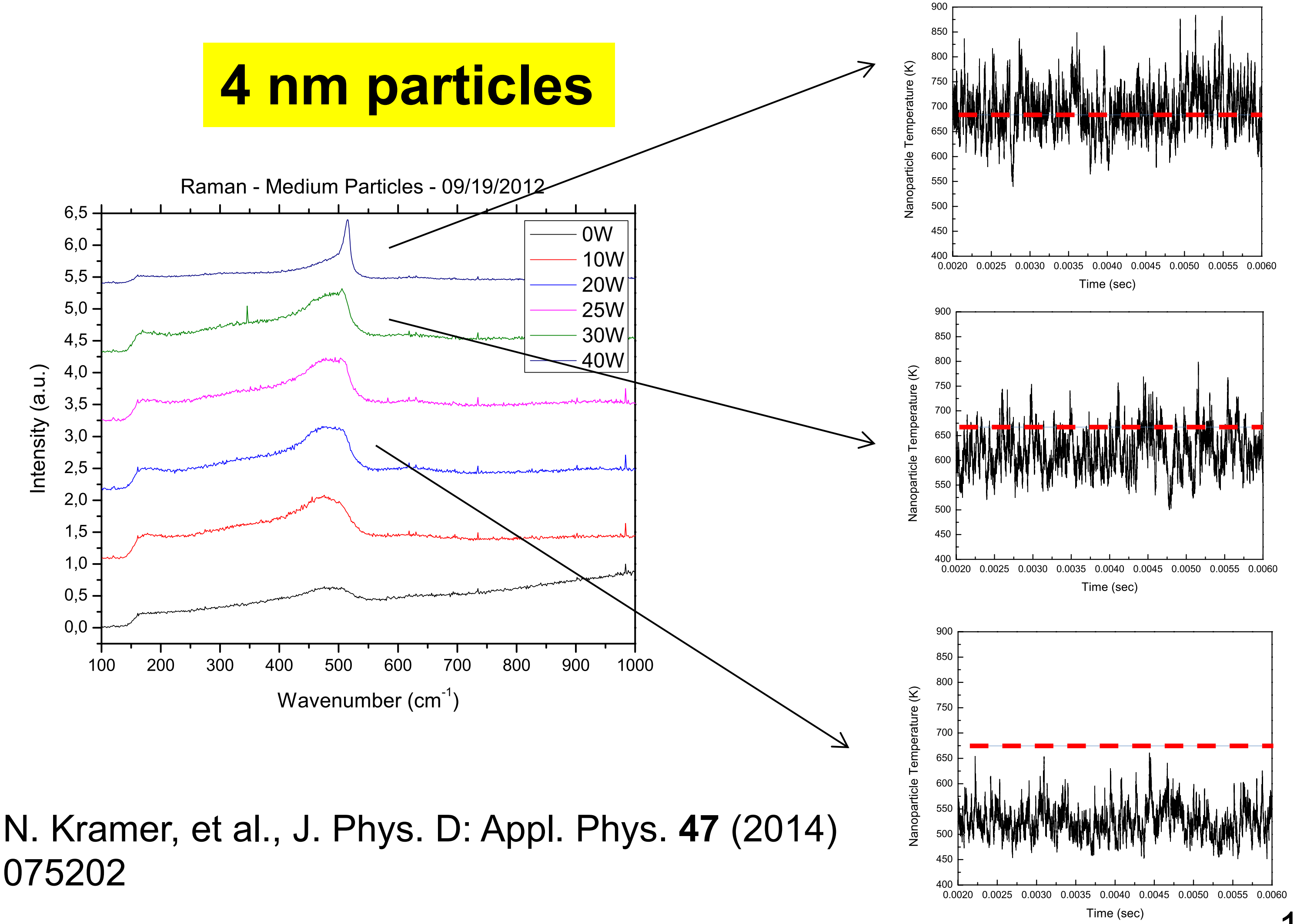


N. Kramer, et al., J. Phys. D: Appl. Phys. **47** (2014) 075202

NP TEMPERATURE VS. POWER

- Electron Temperature: spectroscopy of Ar lines
- Ion Density: capacitive probe
- Hydrogen Density: actinometry of H and Ar lines

4 nm particles



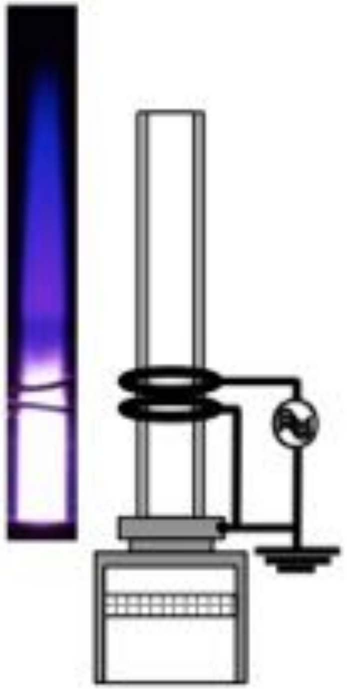
N. Kramer, et al., J. Phys. D: Appl. Phys. **47** (2014) 075202

Why use low pressure plasmas?

- Suited for high melting point materials (IV, III-V NCs)
- Size-control (via residence time)
- Monodispersity (via charging)
- Capable of doped NCs
- Inherently ligand- and solvent-free

Timeline of plasma-synthesized nanocrystals

Plasma Synthesis

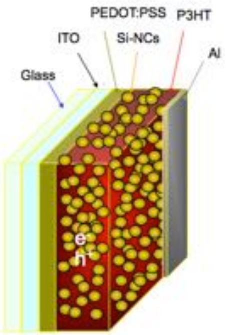


Nano Letters 2005

Si NC PL QY > 60%

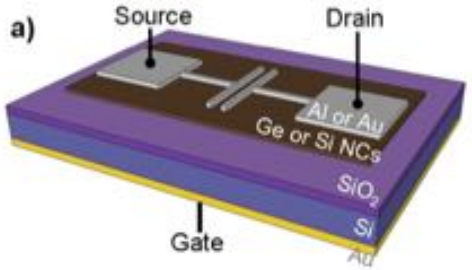
APL 2006
Adv. Func. Mat. 2011

Si NC PV cells



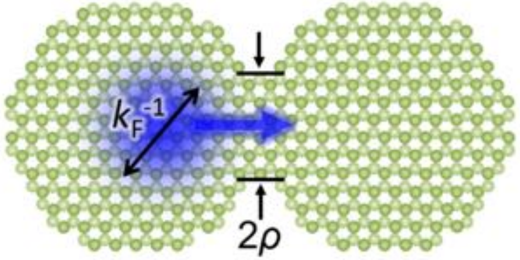
Nano Letters 2009
Adv. Func. Mat. 2010

Si/Ge NC transistors



Nano Letters 2010, 2011

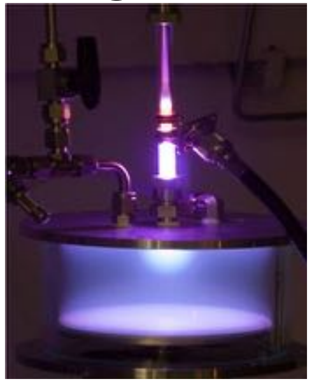
Highly conductive NC films



Nature Commun. 2014
Nature Materials 2016
Science Advances 2019
Nature Materials 2020

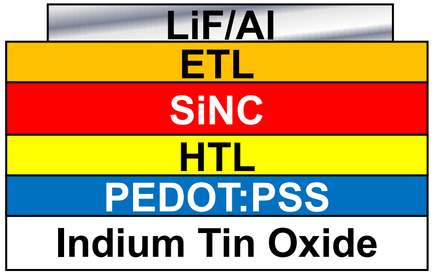
2005 2006 2007 2009 2010 2011 2012 2013 2014 2016 2017 2020

In-flight Si inks



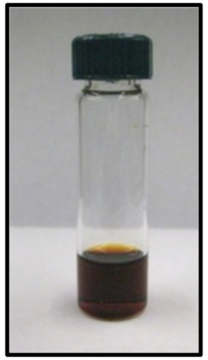
Adv. Mat. 2007

Si NC LED, EQE>9%



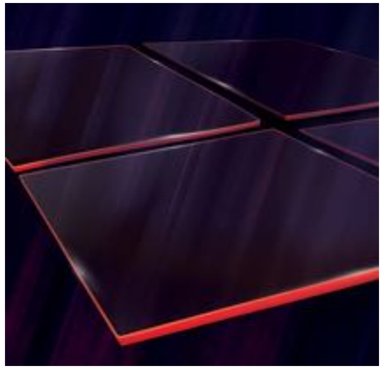
Nano Letters 2010, 2011, 2012

Thermodynamic colloids



Nano Letters 2011, 2018
Nature Commun. 2013

Luminescent Solar Concentrators



Nature Photonics 2017

Plasma produced materials to-date

Plasma-synthesized nanocrystal materials	
Group IV materials	Silicon (Si)[*1], Germanium (Ge)[*2] Silicon-Germanium alloys (SiGe)[*3] Silicon-Carbide
	Phosphorus-doped Si, Ge, SiGe[*4] Boron-doped Si, Ge, SiGe[*5]
Metals	Bismuth (Bi)[*6], Aluminum (Al) † Zinc (Zn) †
Oxides	Zinc Oxide (ZnO)[*7] Aluminum-doped Zinc Oxide (AZO)[*8]
Nitrides	Titanium Nitride (TiN)[9, †] Gallium Nitride (GaN)[*10] Silicon Nitride (SiN)†
Phosphides	Indium Phosphide (InP)[*11]
Sulfides	Copper Sulfide (Cu_2S)[*12] Zinc Sulfide (ZnS)[*13] Tin Sulfide (SnS)[*13]

Current research projects:

- Si: PV
- Si, Ge: bioimaging
- ZnO: TCOs
- Al_2O_3: structural materials
- TiO_2: photocatalysis
- MoS_2: catalyst for H_2
- C-Ru: catalyst for NH_3

http://www.dupont.com/products-and-services/solar-photovoltaic-materials/silicon-inks.html

Samantha Ehrenberg

Francesco Meinardi

Sergio Brovelli

Semitransparent solar luminescent concentrators

Meinardi, Ehrenberg, Dhamo, Carulli, Mauri, Simonetti, Kortshagen, Brovelli, *Nature Photonics* ***11***, 177 (2017)

Silicon: Bulk vs. Quantum Dots

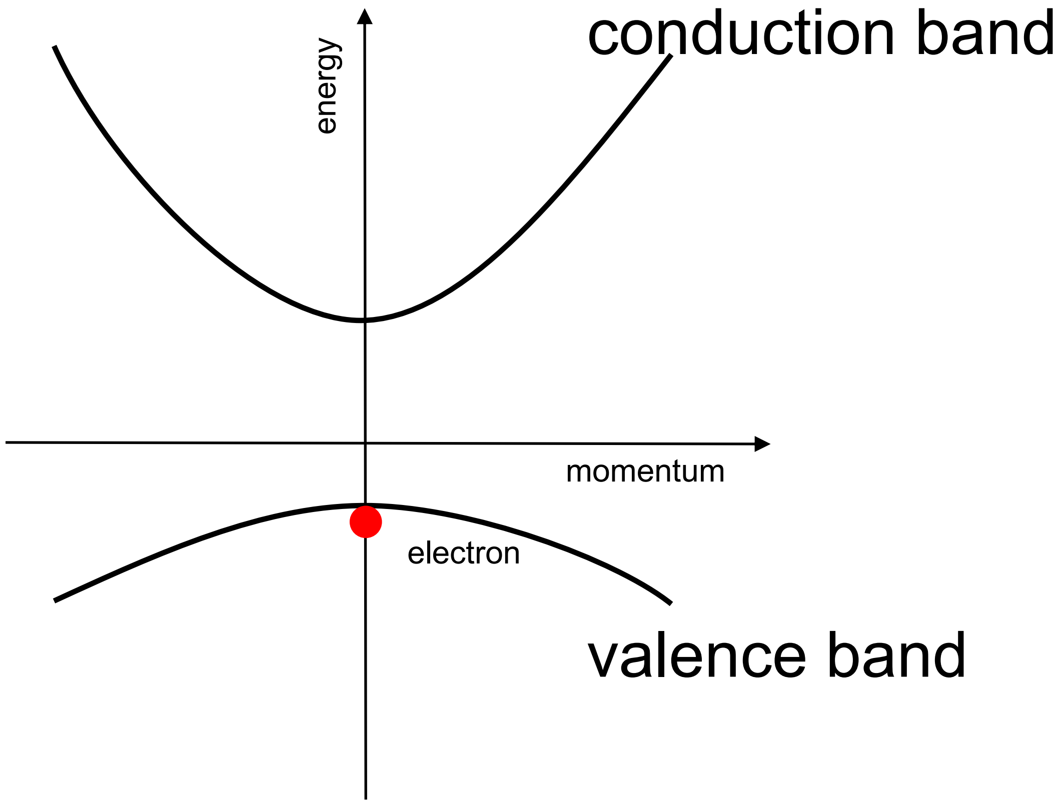
UV source OFF
Room light ON

UV source ON
Room light ON

UV source ON
Room light OFF

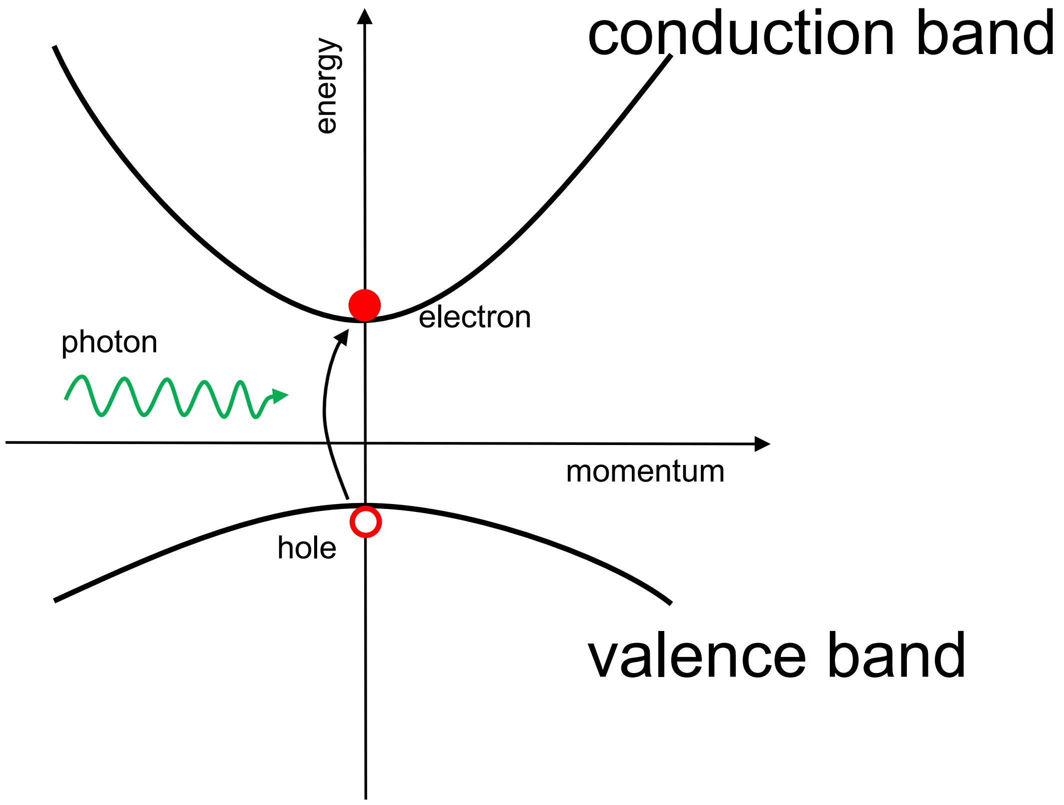
Visible emission due to quantum confinement

Direct vs. indirect band gap semiconductor



direct band gap
“good light emitters”
(e.g. GaN)

Direct vs. indirect band gap semiconductor



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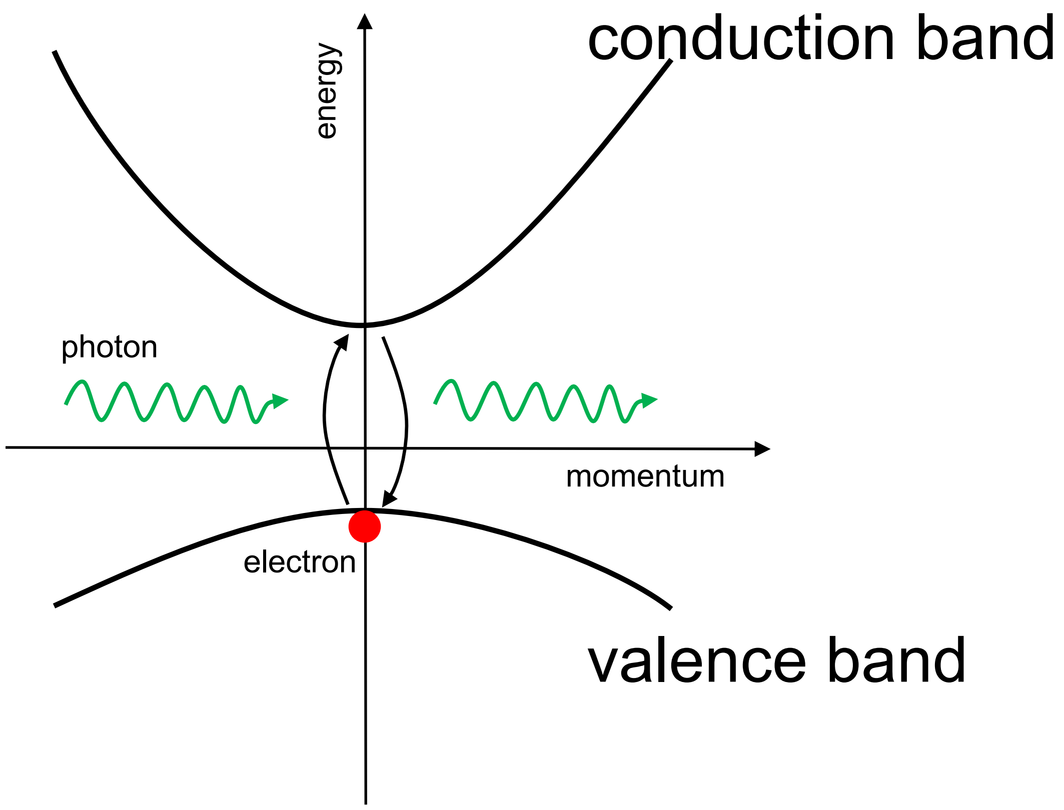
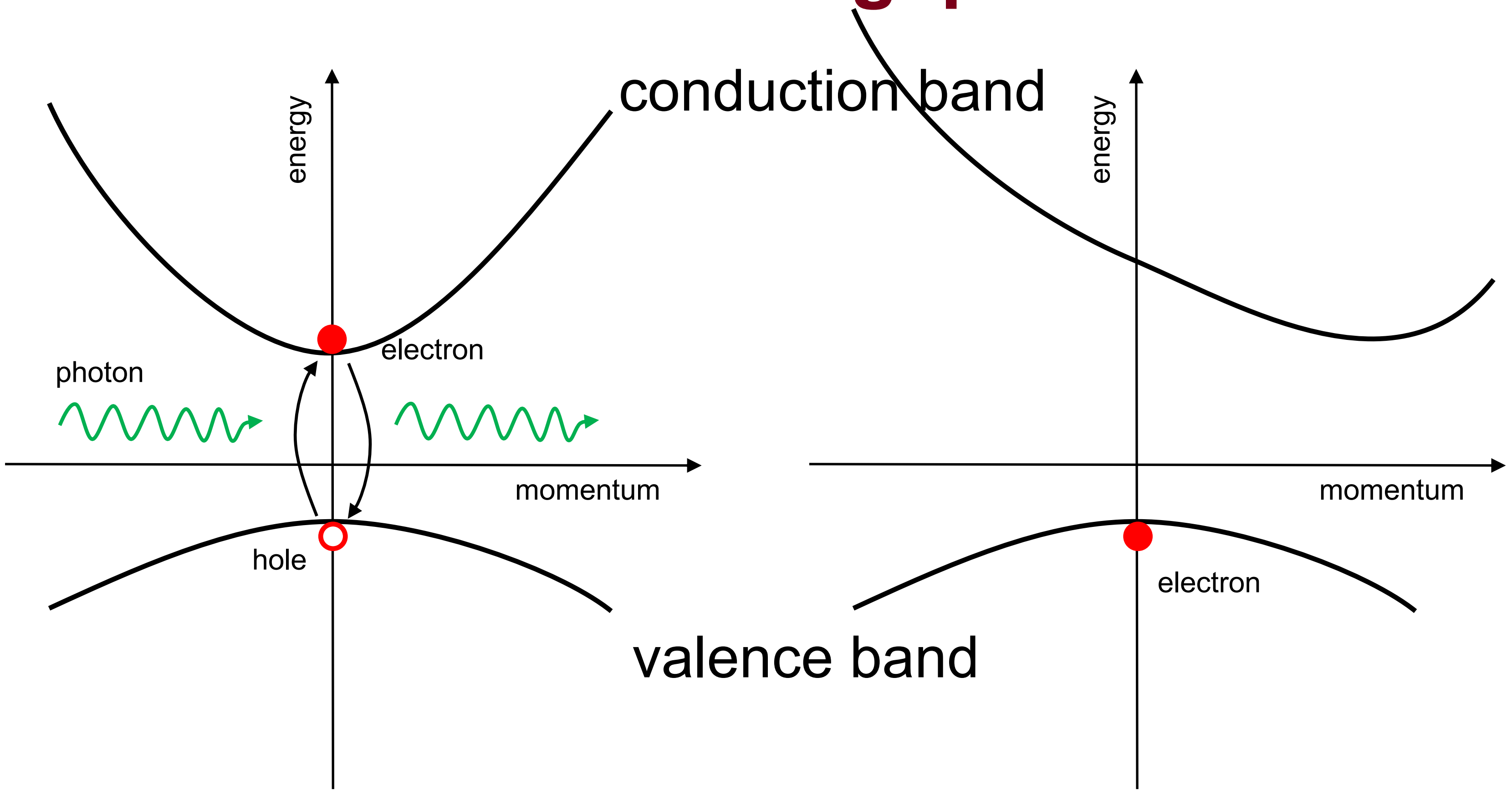
Direct vs. indirect band gap semiconductor



direct band gap
“good light emitters”
(e.g. GaN)

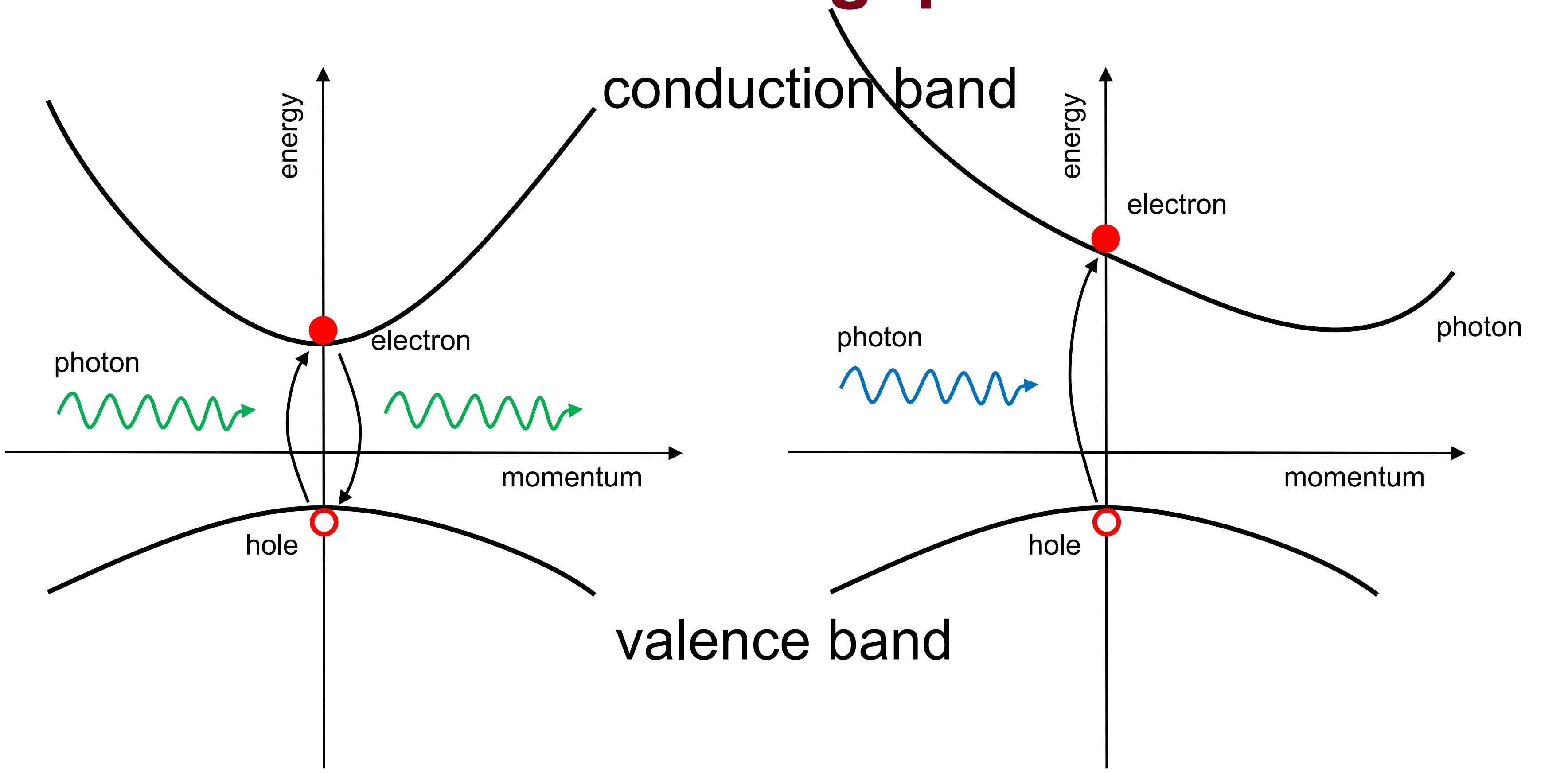
Direct vs. indirect band gap semiconductor



direct band gap
"good light emitters"
(e.g. GaN)

indirect band gap
"poor light emitters"
(e.g. Silicon)

Direct vs. indirect band gap semiconductor



direct band gap
“good light emitters”
(e.g. GaN)

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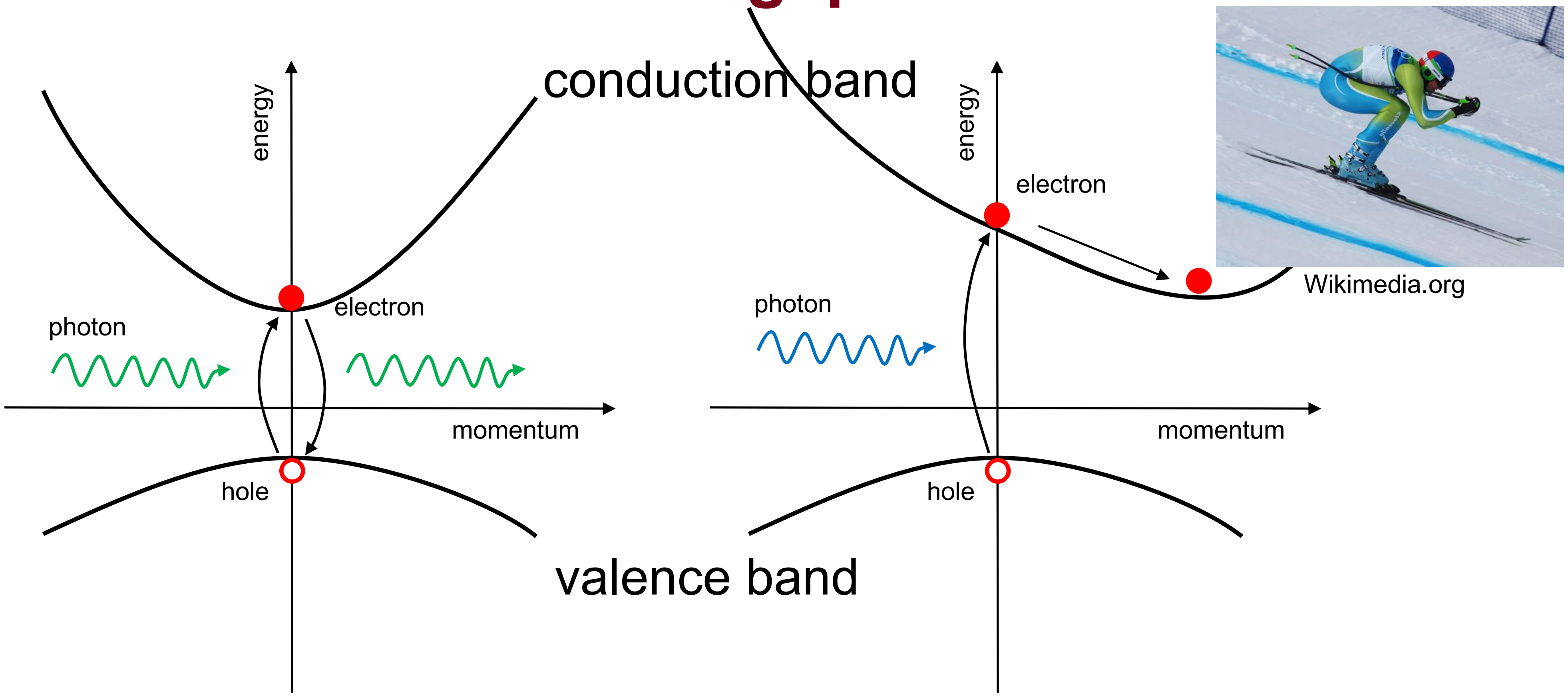
(e.g. Silicon)

Direct vs. indirect band gap semiconductor

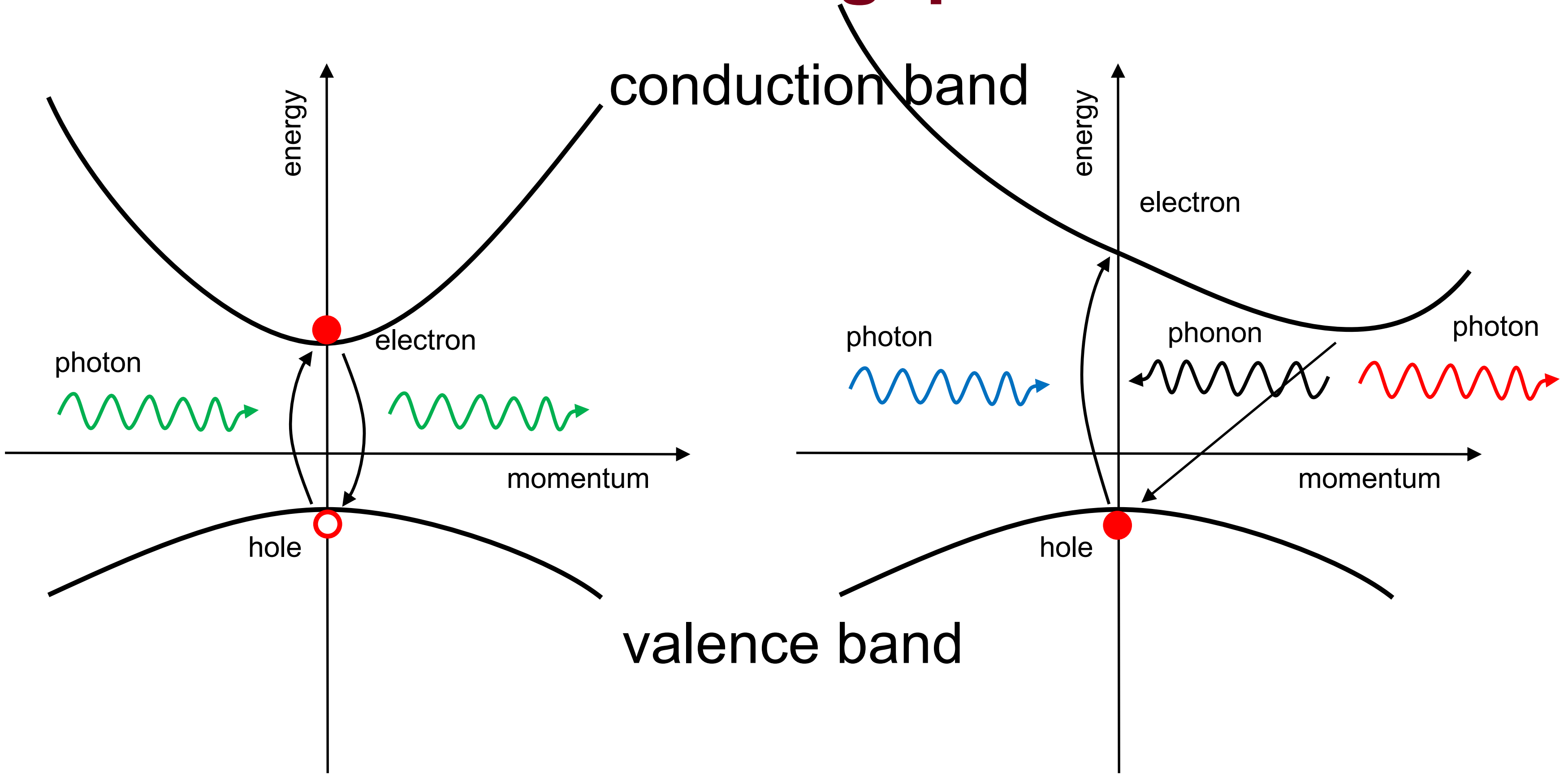


Wikimedia.org

direct band gap
"good light emitters"
(e.g. GaN)

indirect band gap
"poor light emitters"
(e.g. Silicon)

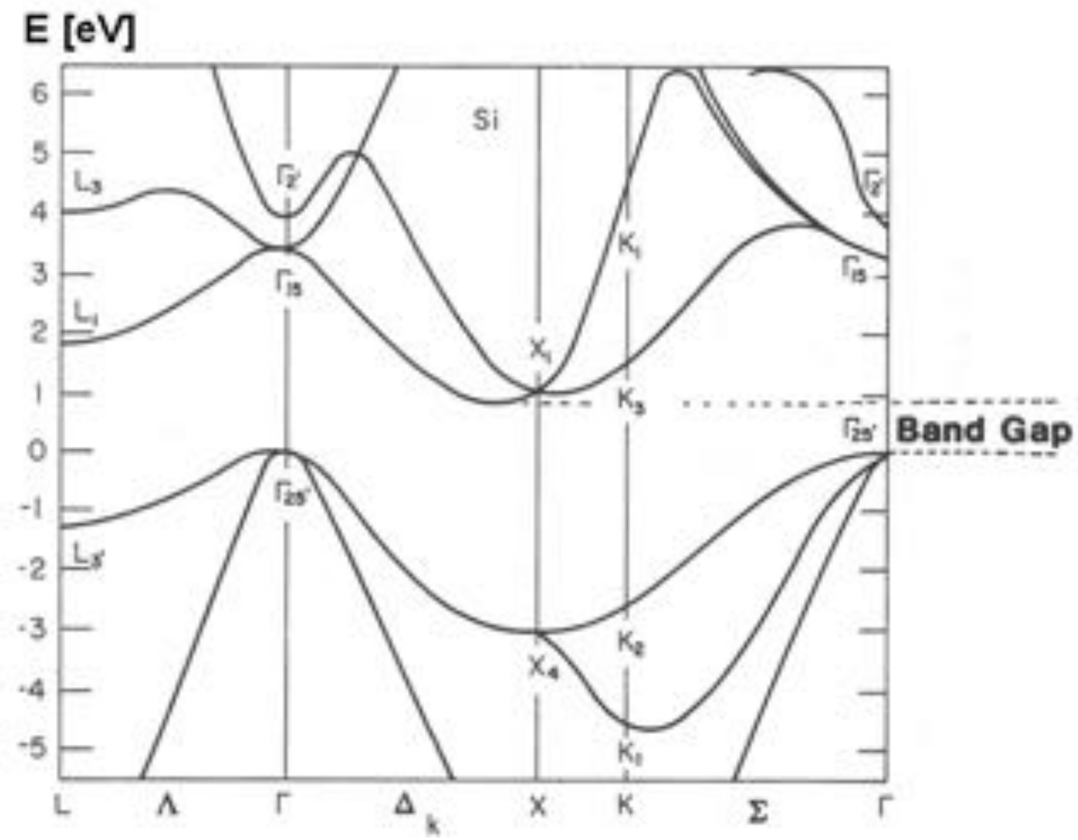
Direct vs. indirect band gap semiconductor

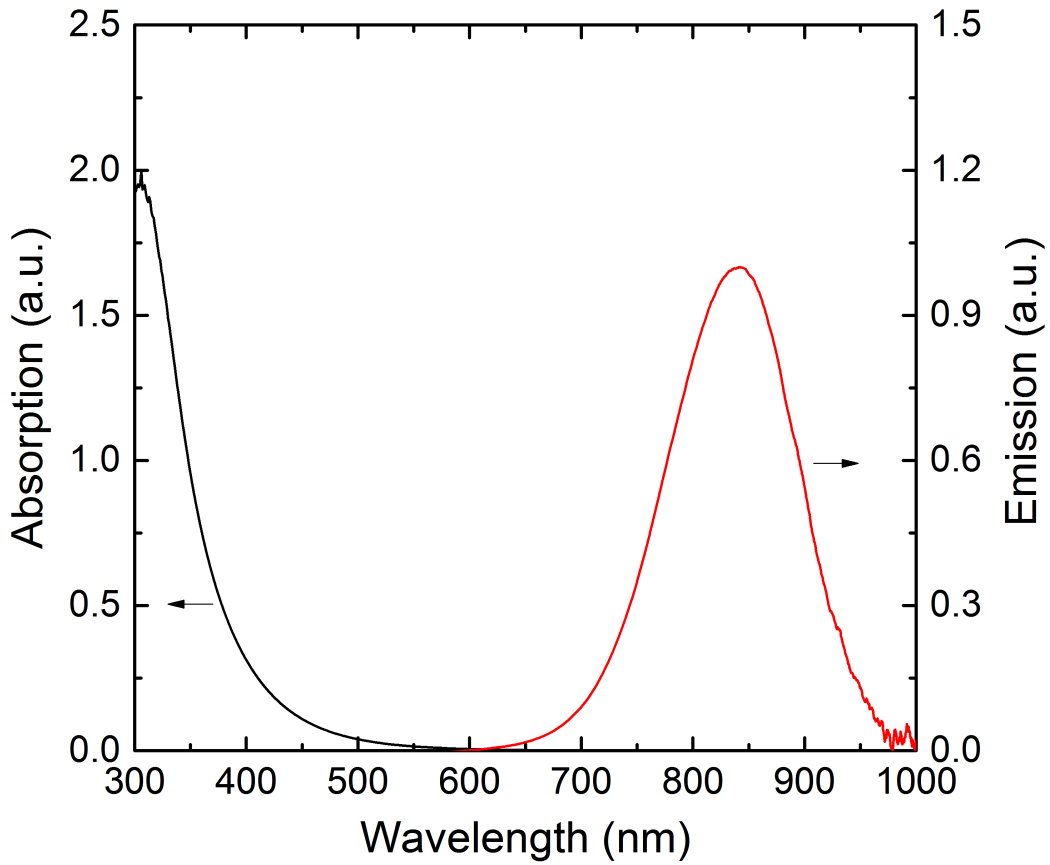


direct band gap
“good light emitters”
(e.g. GaN)

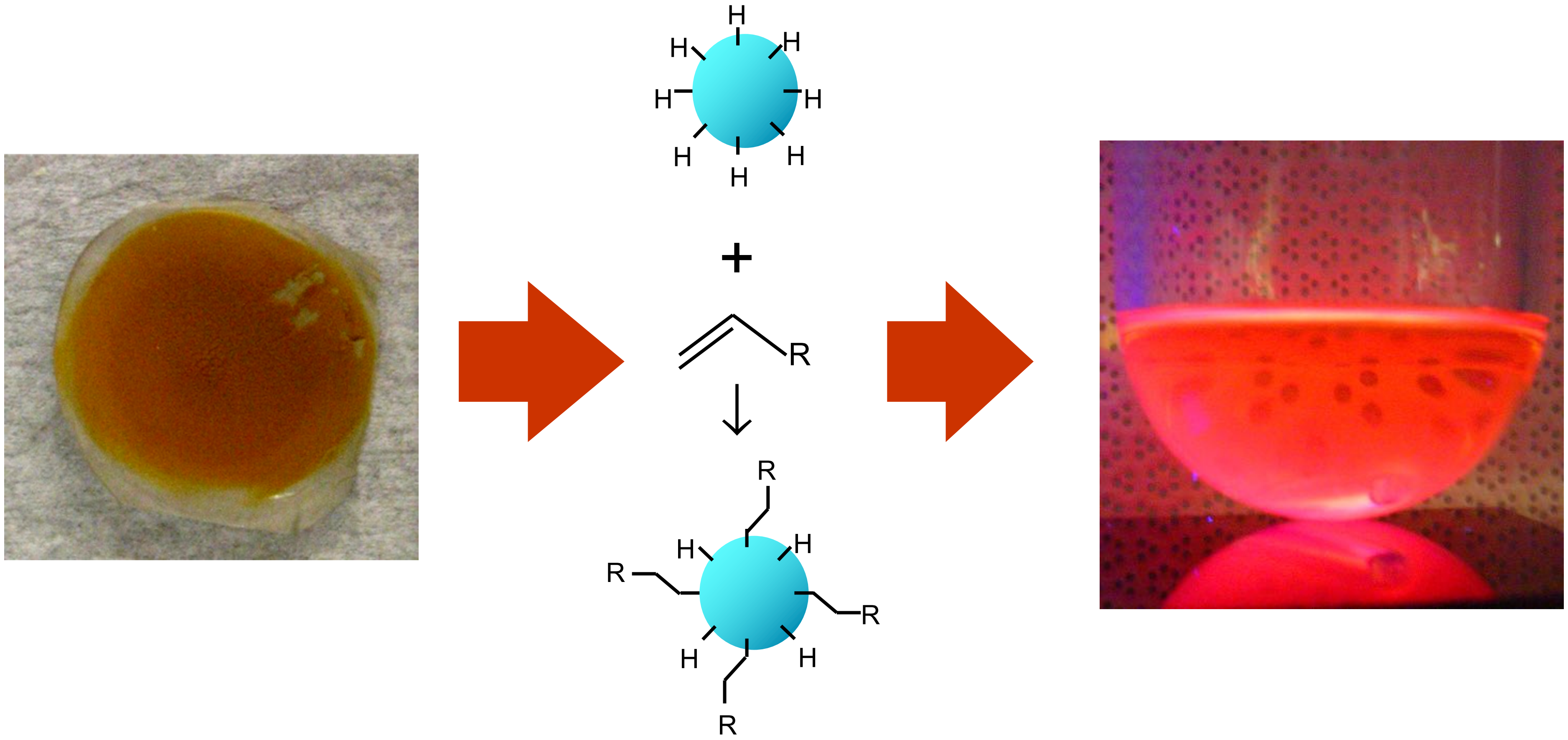
indirect band gap
“poor light emitters”
(e.g. Silicon)

Si QDs: Indirect band gap = inherent Stokes shift





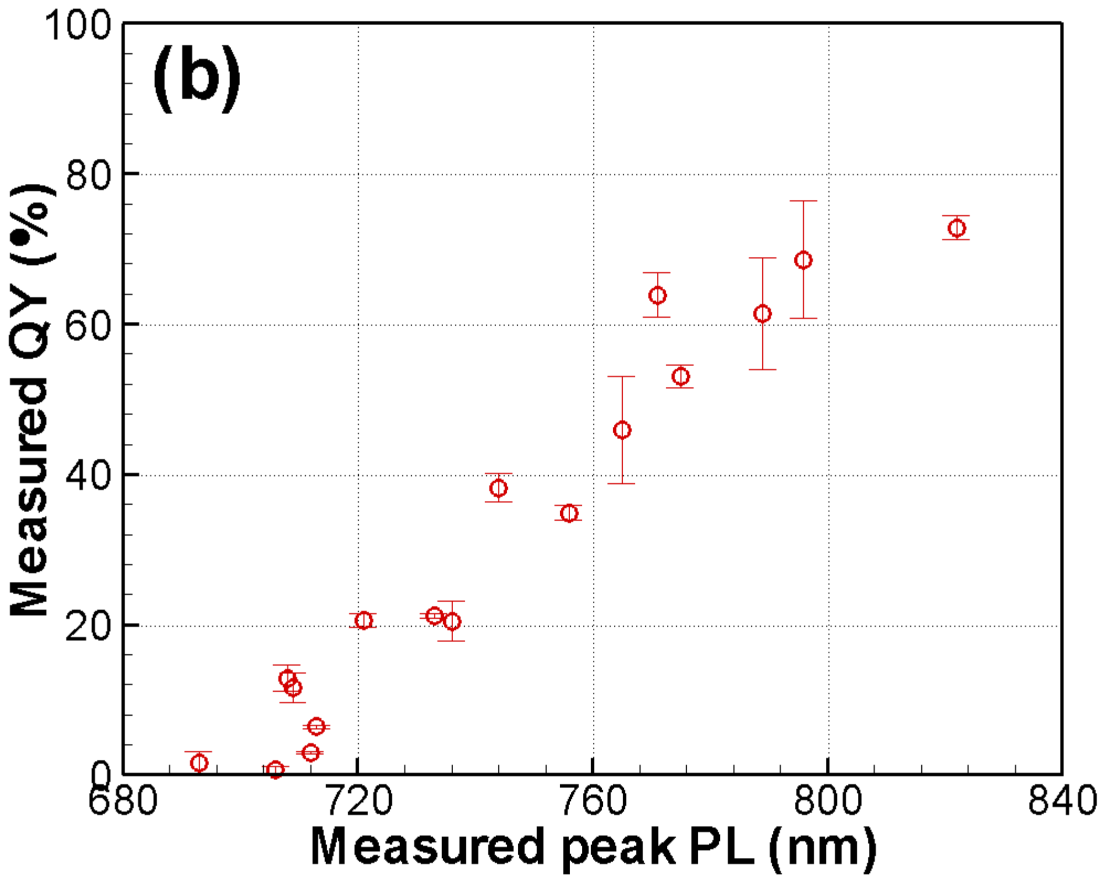
Luminescent Si nanocrystals



Ligands: octadecene,
dodecene, styrene, …

Jurbergs et al., Appl. Phys. Lett., 2006

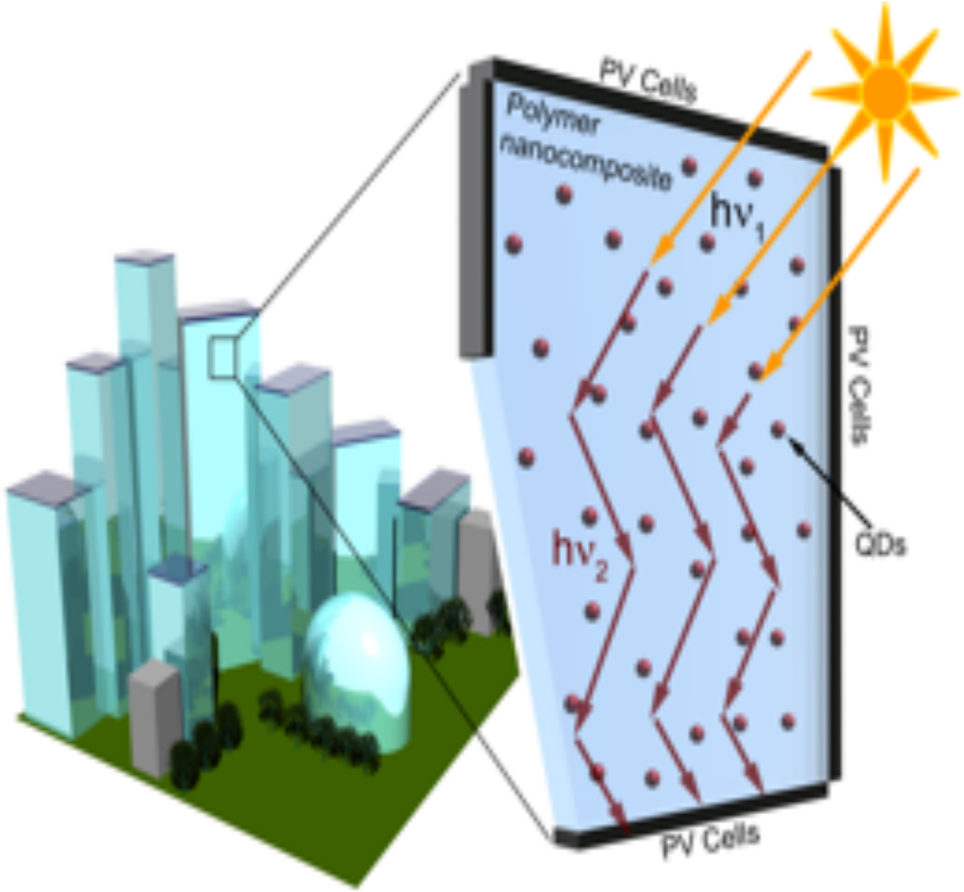
Si NC ensemble quantum yield



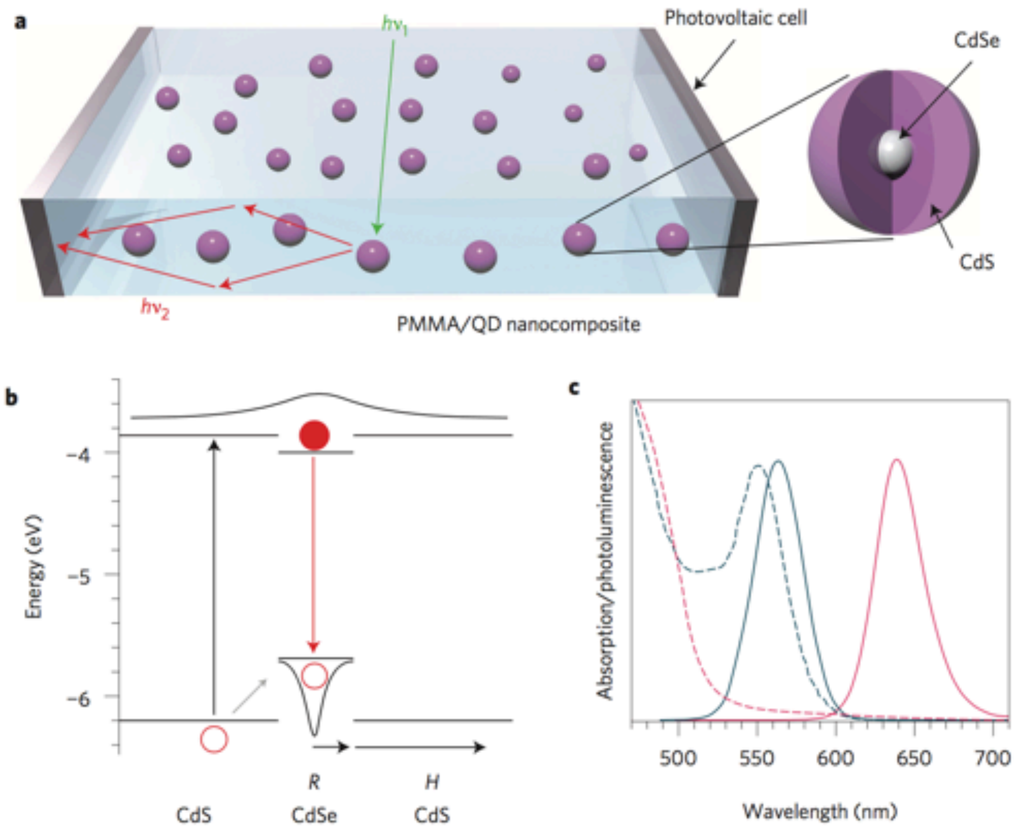
Jurbergs et al., Appl. Phys. Lett., 2006

Mangolini et al., Phys. Stat. Solid C, 2007

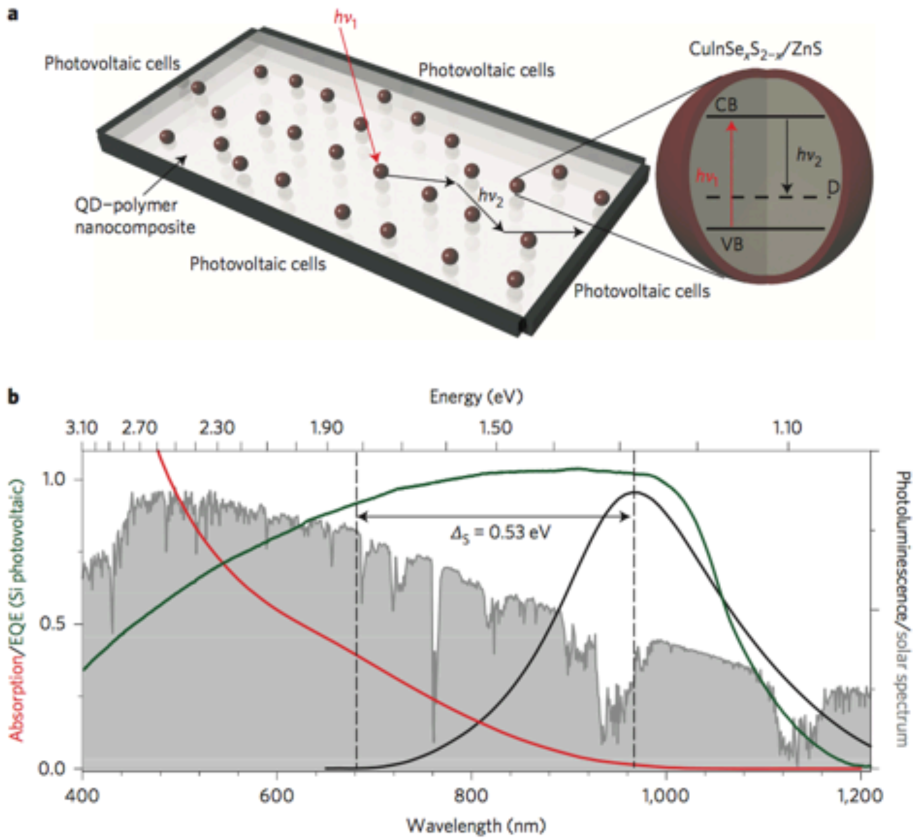
LSC for building integrated PV



Previous transparent LSC work

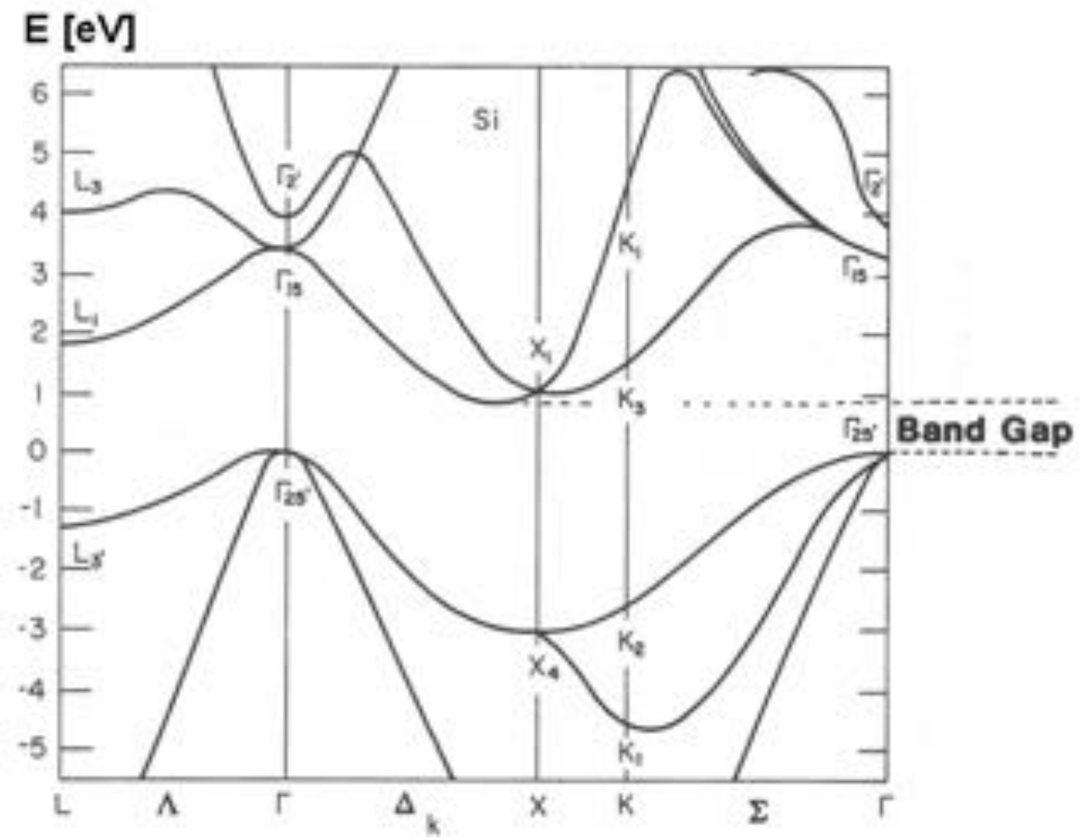


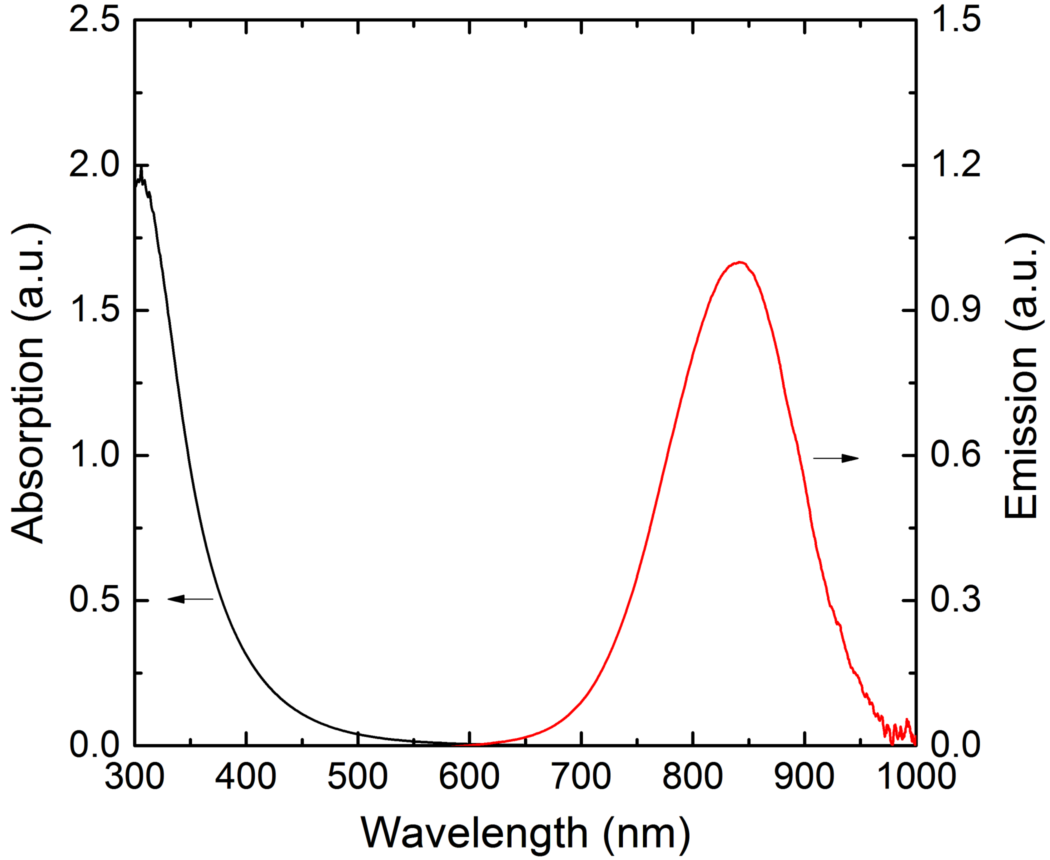
F. Meinardi, *et al., Nature Photonics* (2014)



F. Meinardi, *et al.*, *Nature Nanotech.* (2015)

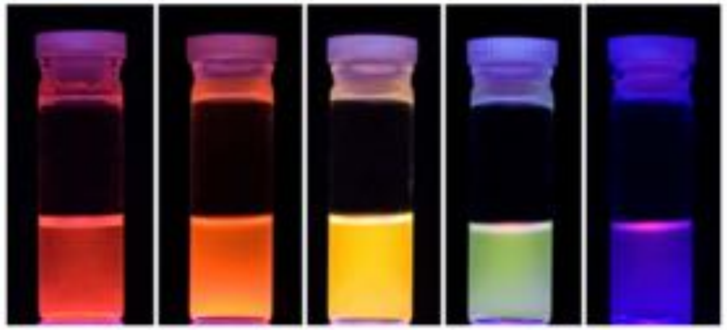
Si QDs: Indirect band gap = inherent Stokes shift





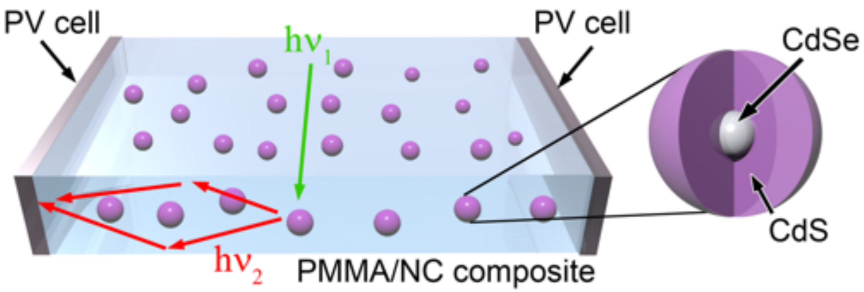
Si quantum dot polymer LSCs

Si Quantum Dots

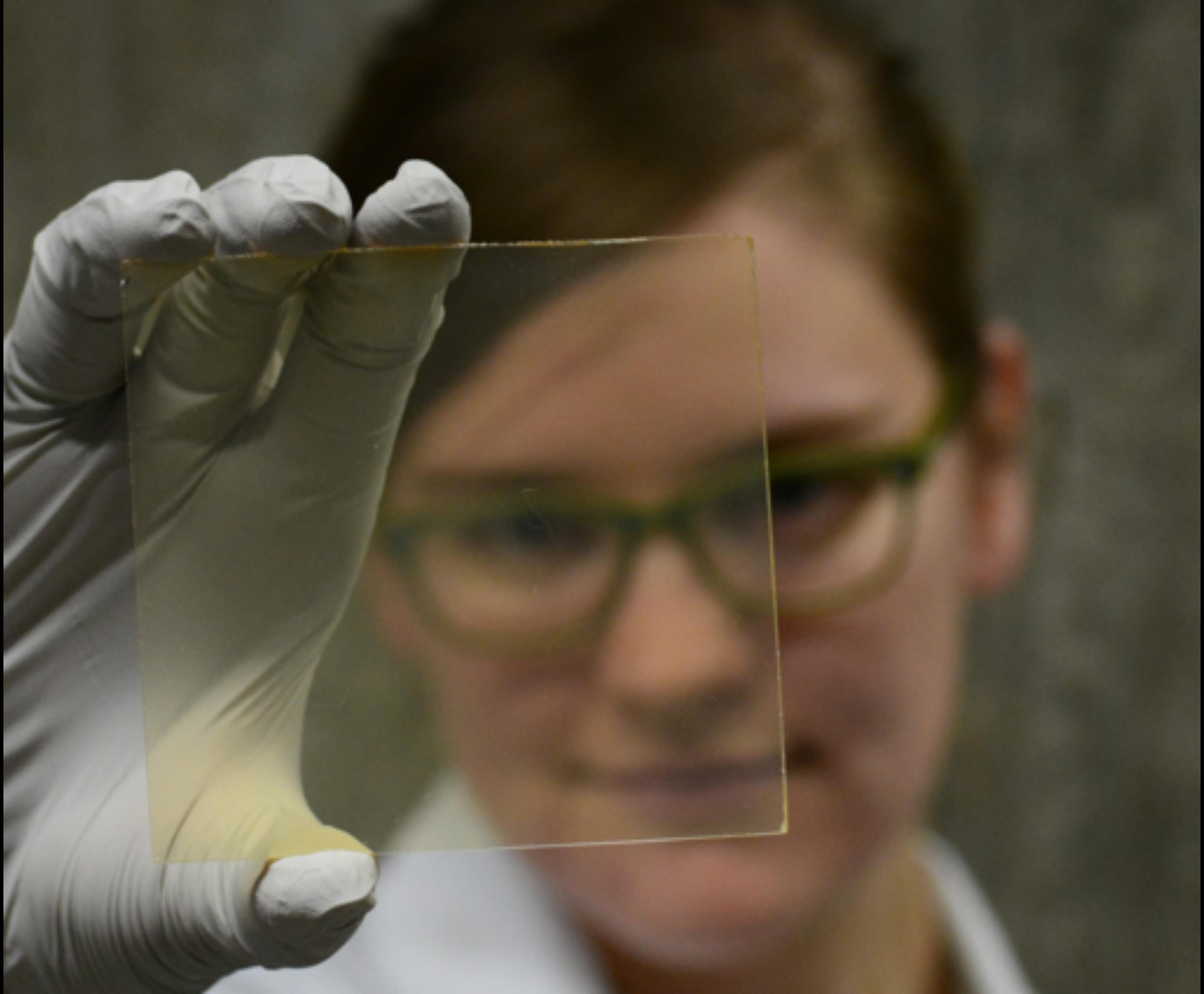


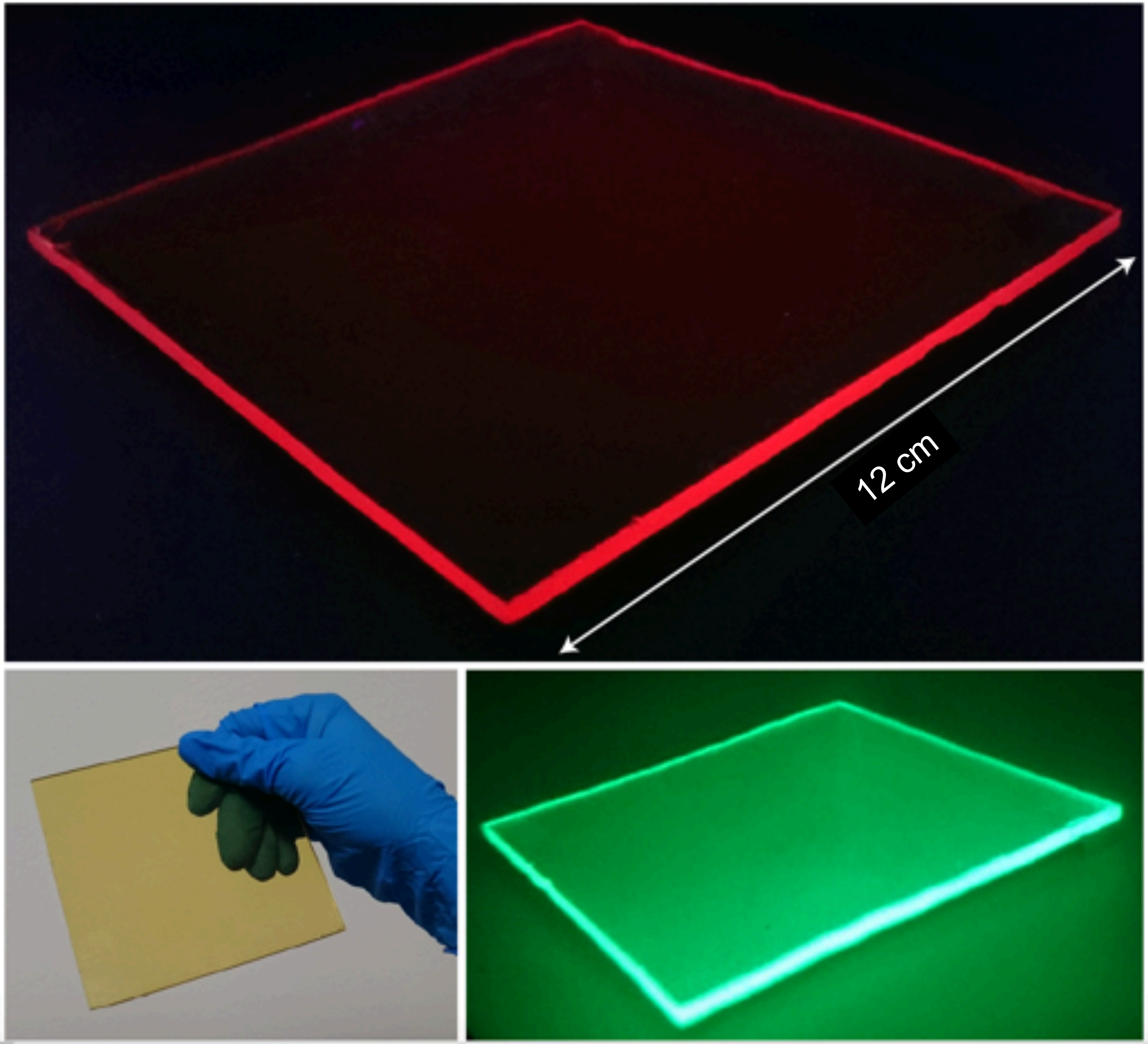
X.D. Pi, S. A Campbell, and U. Kortshagen, *Nanotechnology* **19**, 245603 (2008).

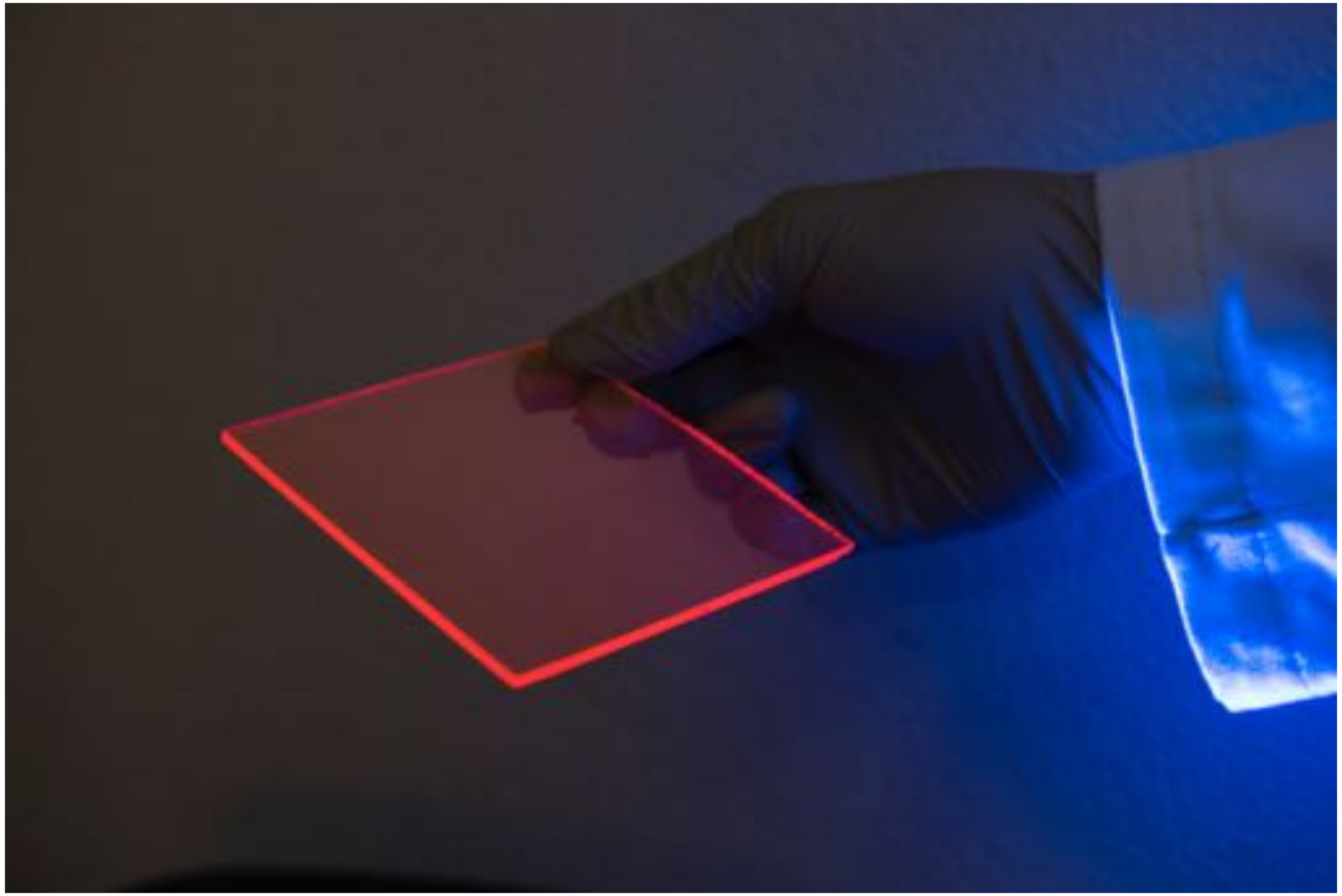
Quantum Dot LSCs



F. Meinardi, *et al., Nature Photonics* (2014)
F. Meinardi, *et al.*, *Nature Nanotech.* (2015)



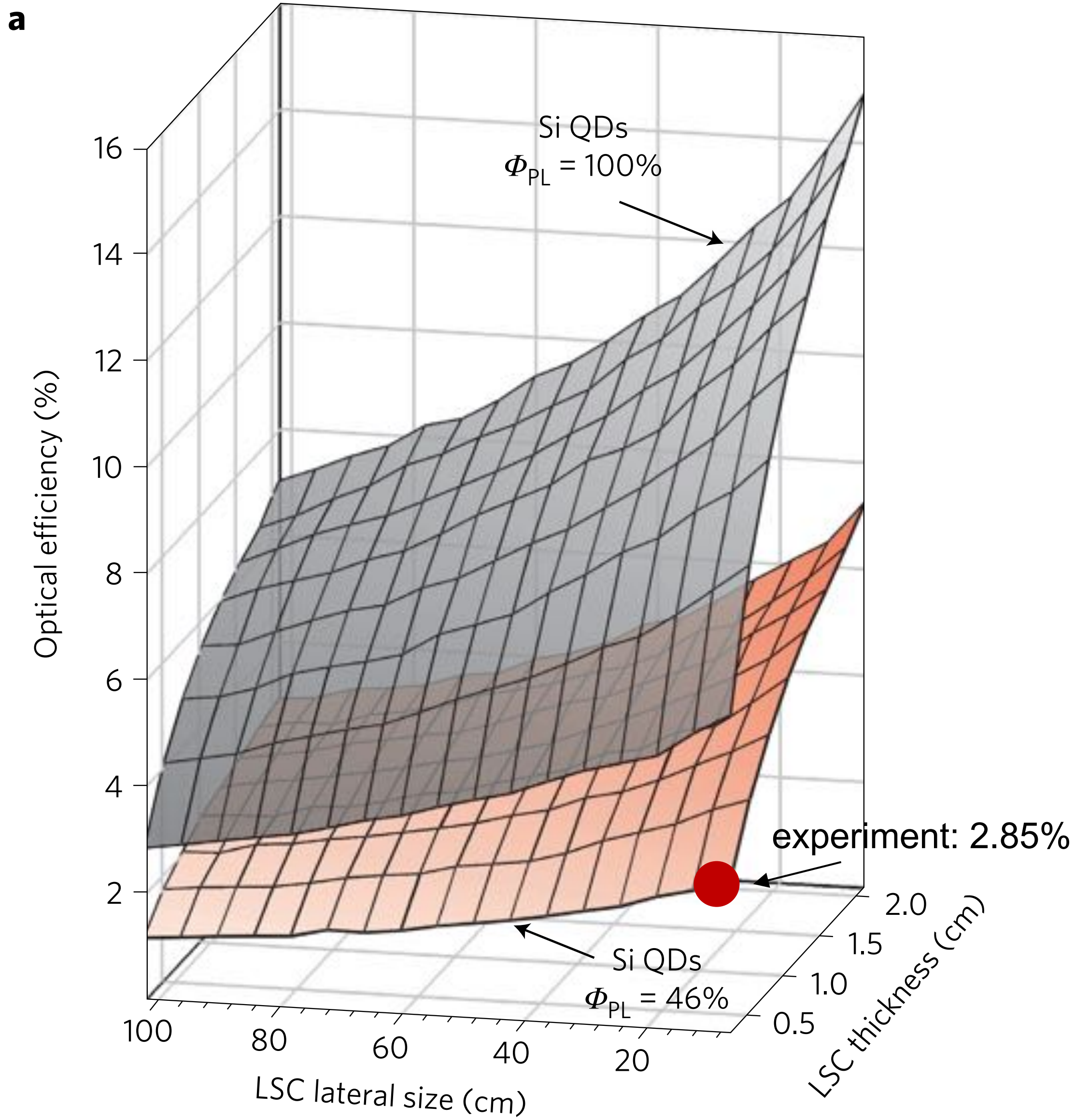

12 cm



polymer matrix: poly lauryl metharyclate (PLMA) (n=1.49)
optical conv. eff.: $\eta = P_{out} / P_{in} = 2.85\%$
quantum efficiency: $\eta_Q = N^{ph}_{out} / N^{ph}_{in} = 30\%$
light trapping eff.: $\eta_{tr} = (1-1/n^2)^{1/2} = 74.1\%$

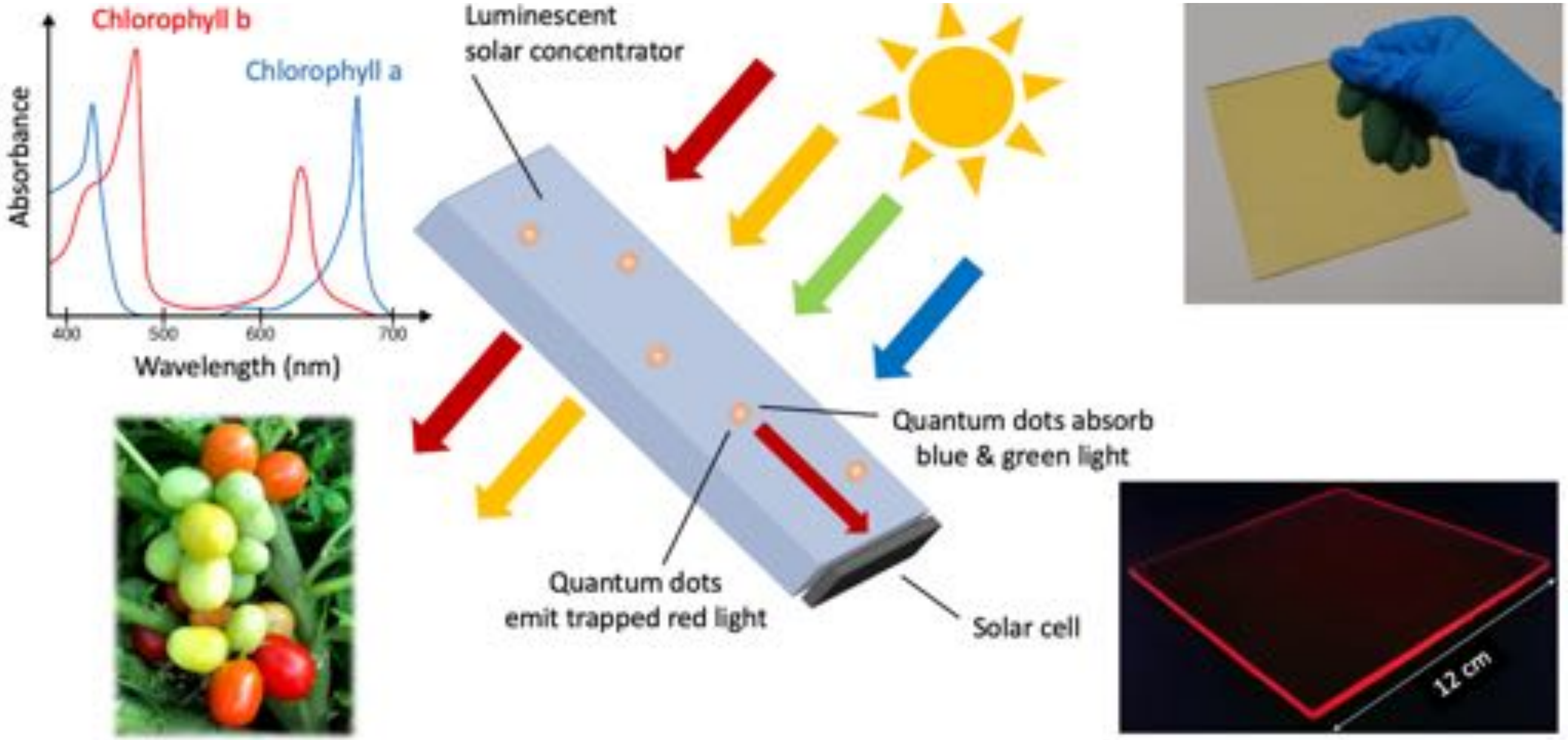
Meinardi, Ehrenberg, Dhamo, Carulli, Mauri, Simonetti, Kortshagen, Brovelli, *Nat. Photon.* ***11***, 177 (2017)

Monte Carlo-ray tracing

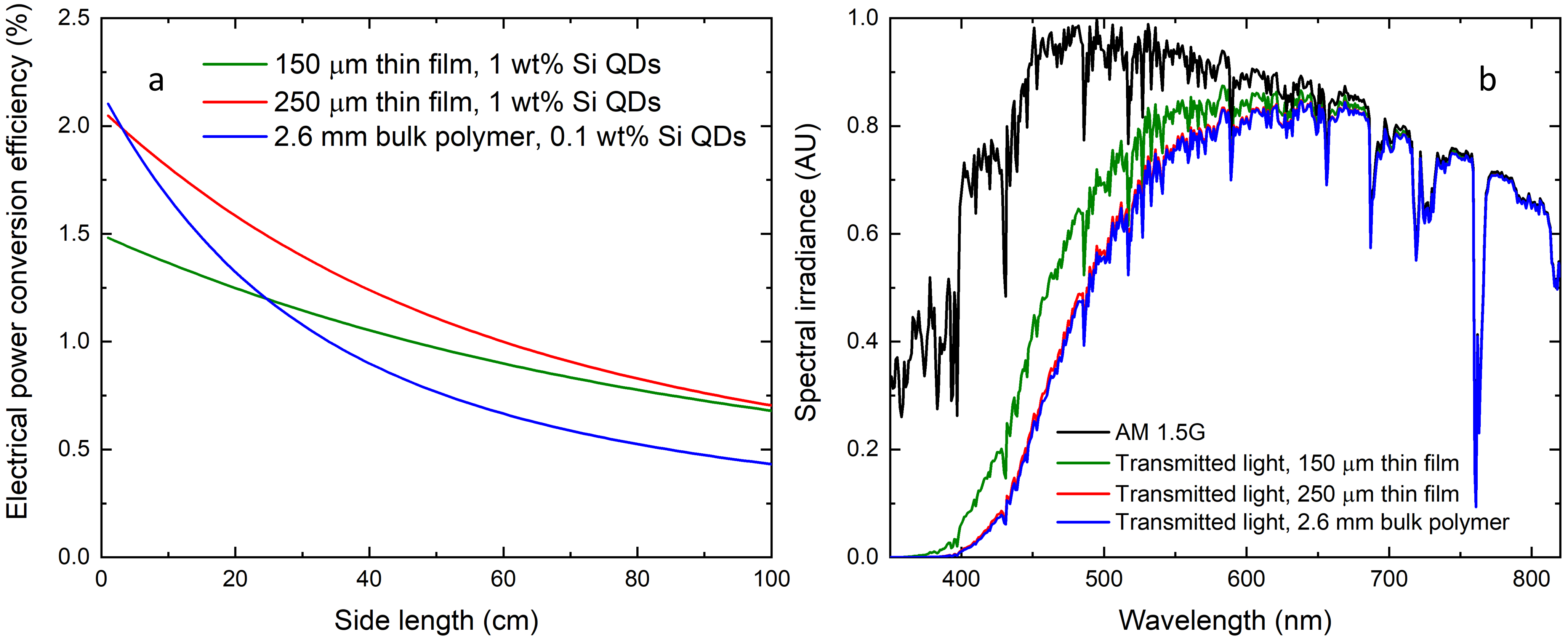


Meinardi, Ehrenberg, Dhamo, Carulli, Mauri, Simonetti, Kortshagen, Brovelli, *Nat. Photon.* ***11***, 177 (2017)

Silicon LSCs in agriculture



Power conversion efficiency and transmission



Levelized Cost of Energy

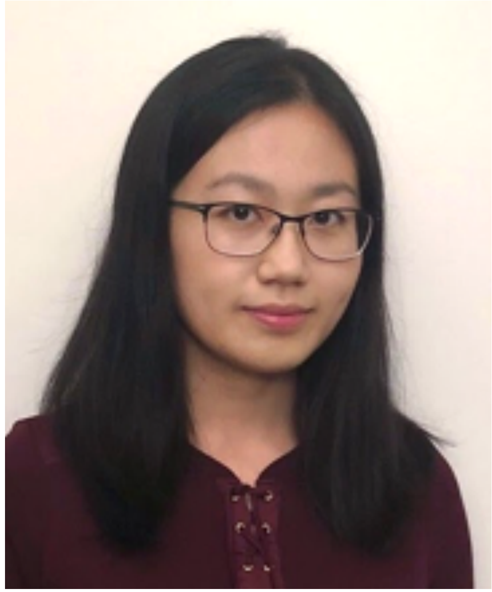
$$LCOE = \frac{\text{cost of system}}{\text{electricity produced over life}}$$

DOE 2030 target: 3¢/kWh

Cost of 1 kg Si QD in 100 kg PMMA		Current recipe mass (kg)	Current recipe cost ($)	Target recipe mass (kg)	Target recipe cost ($)
Plasma Synthesis	Argon ($0.24/kg)	100	24	100	24
	Hydrogen ($2.30/kg)	10	23	10	23
	Silane ($10/kg)	1	10	1	10
Surface Functionalization	Mesitylene ($1.80/kg)	800	1440	9	16
	10-undecenoic acid ($1/kg)	200	200	2	2
	hexane ($1/kg)	1000	1000	0	0
PMMA matrix	radical initiator ($2/kg)	1	2	1	2
	MMA ($2.3/kg)	100	230	100	230
Manufacturing	nonmaterials costs ($16/kg	1	16	1	16
cost to produce 1 kg of Si QDs in 100 kg PMMA matrix			**2945**		**323**

Cost to produce a 1m x 1m SiQD LSC	cost ($)	cost ($)
2g of Si QDs in 200g PMMA	5.89	0.65
borosilicate glass / sqm	1.00	1.00
other materials / sqm	1.00	1.00
total cost of 1 sqm Si QD LSC	**7.89**	**2.65**
	1.6¢/kWh	0.6¢/kWh

At 0.7% PCE
a 1x1 m^2 Si LSC window
in Minnesota would
produce **480 kWh**
of electricity over 30 yrs.

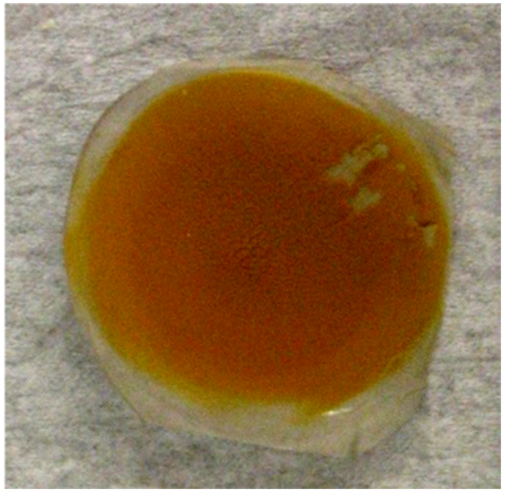


Zhaohan Li

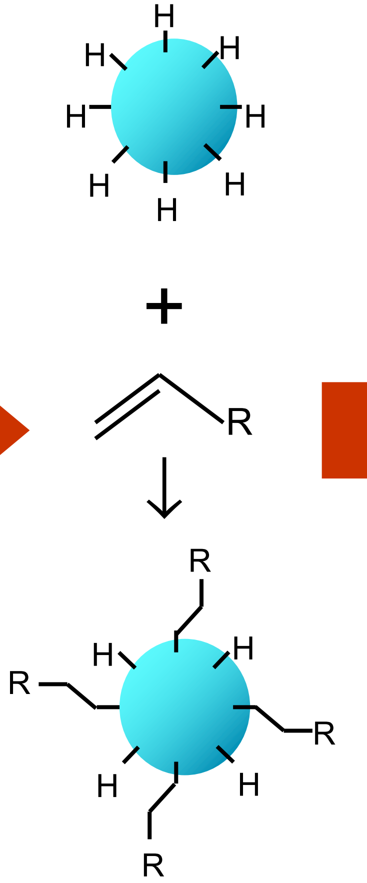
Toward all-gas-phase processing of quantum dots

Zhaohan Li and U. Kortshagen, Chemistry of Materials, **31 (20)**, 8451-8458 (2019)

Disadvantages or liquid phase post-processing



Ligand termination
PLQY < 5%



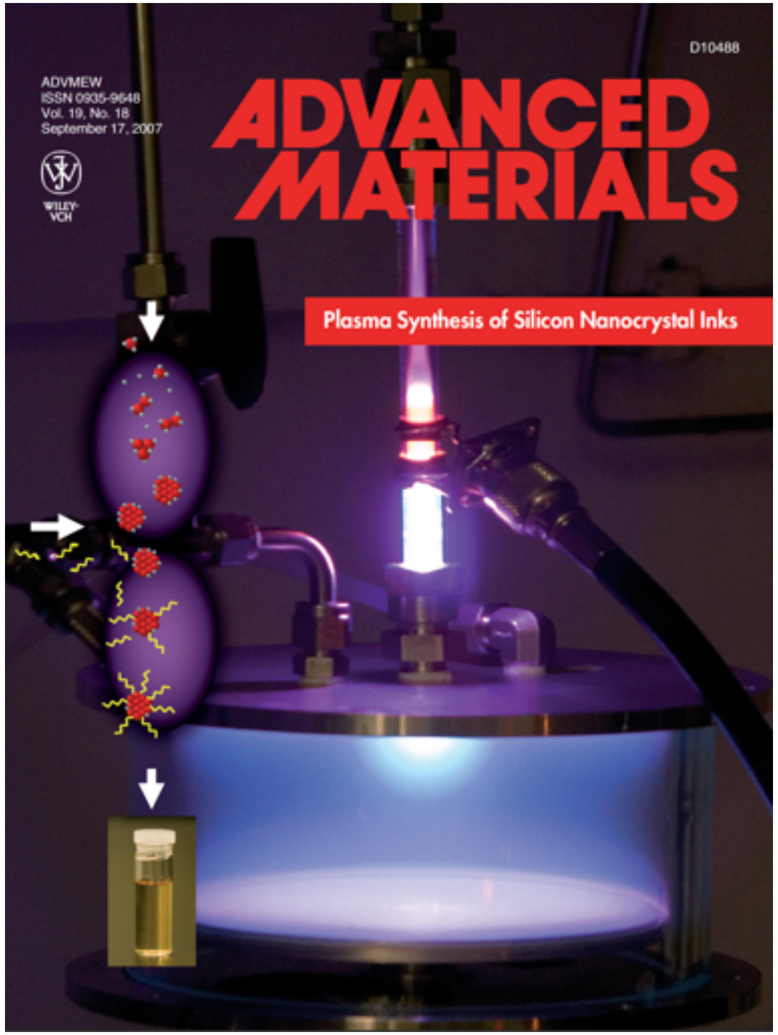
Ligands: octadecene, dodecene, styrene, …

Ligand termination
PLQY ~50%

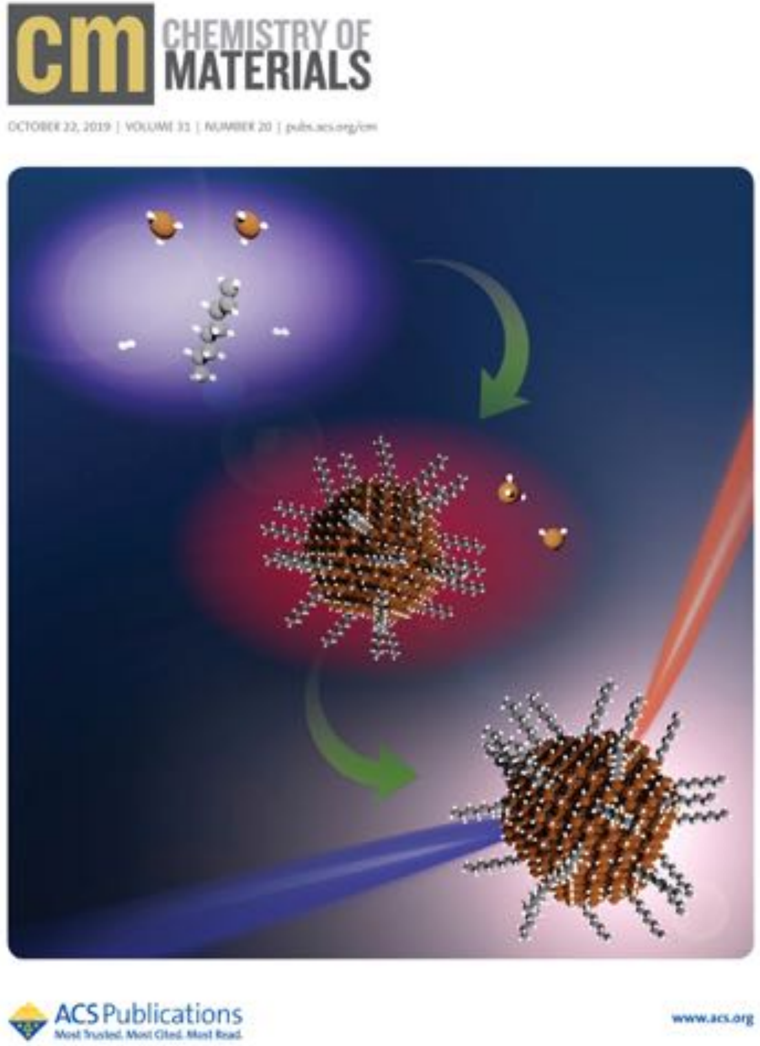
- Batch process
- Slow: up to 24 hrs
- Requires solvents
- Not “green chemistry”

Jurbergs et al., Appl. Phys. Lett., 2006

Toward all-gas-phase processing of quantum dots

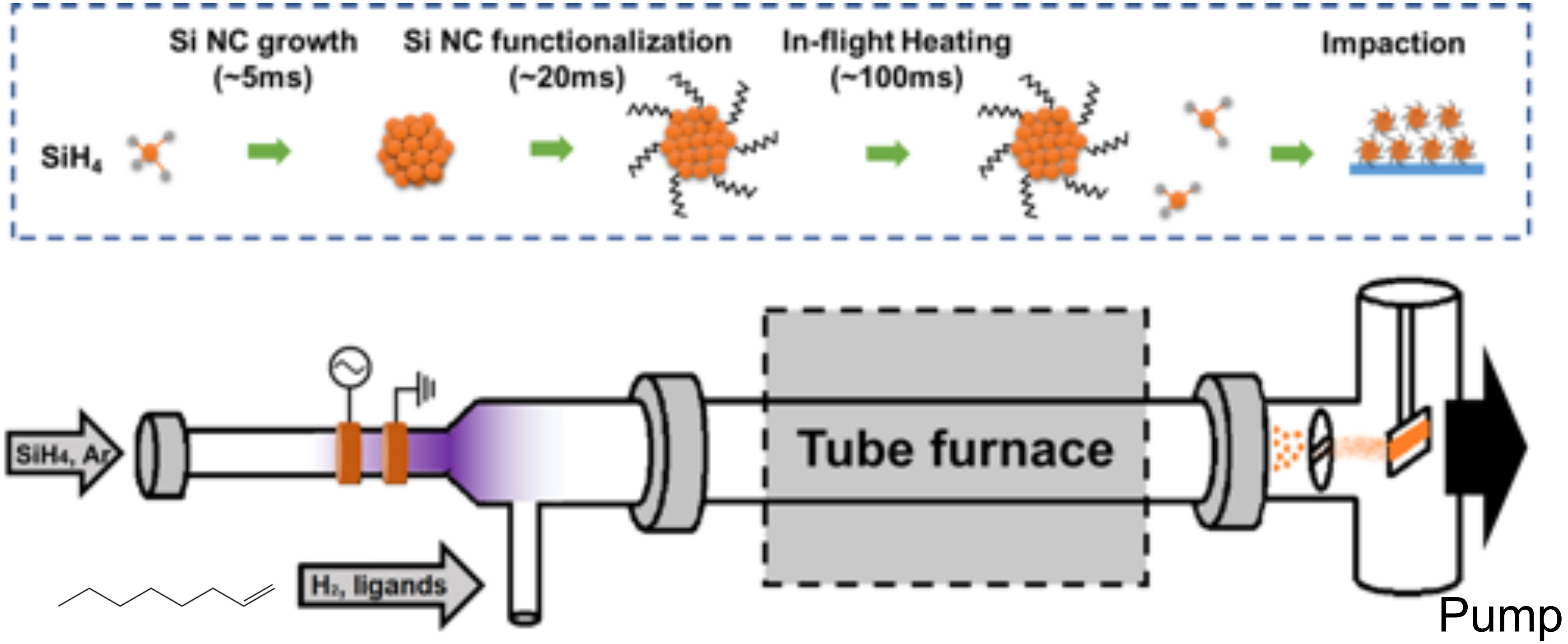


Lorenzo Mangolini



Zhaohan Li

Experimental Setup

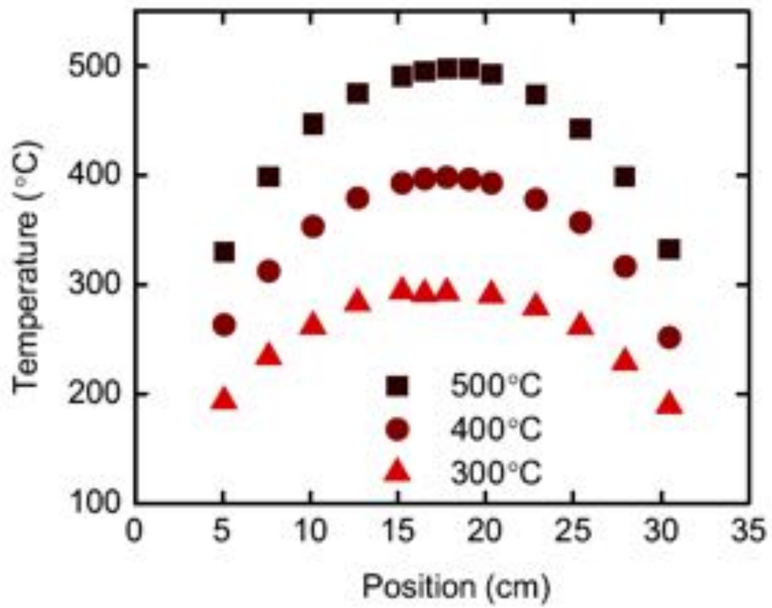


Pressure	2.2-2.6 Torr
RF Power	13.56 MHz
Ar	30 sccm
SiH_4/He	14 sccm
H_2	100 sccm
Ligand(1-octene)	18 sccm

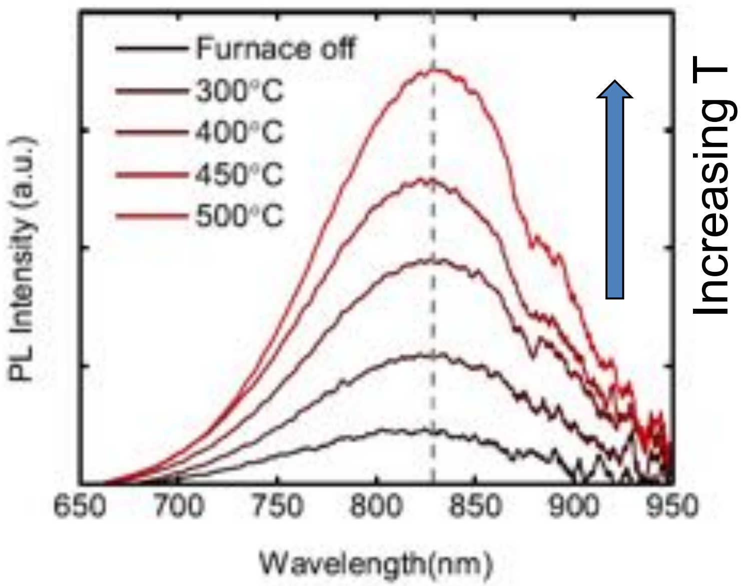
- Continuous synthesis of luminescent silicon nanocrystals
- Si NCs diameters 3.2 ± 0.5 nm and emission peak at 828 nm

Influence of Processing Temperature on Photoluminescence

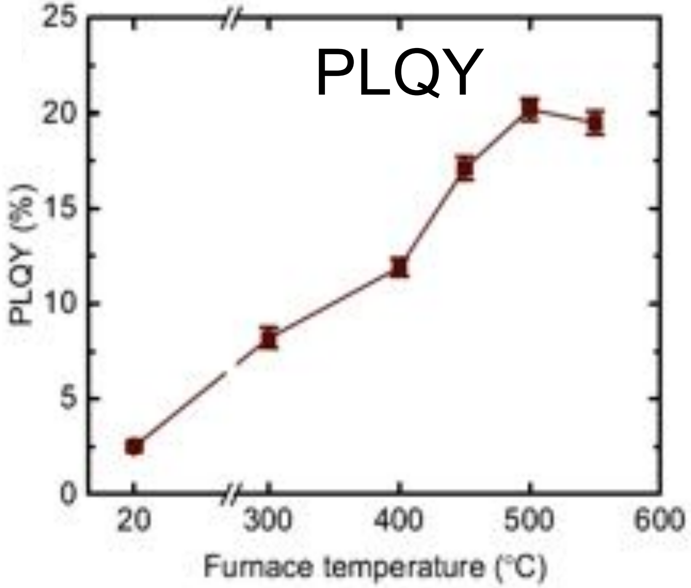
Furnace temperature profile



Residence time ~ 100 ms

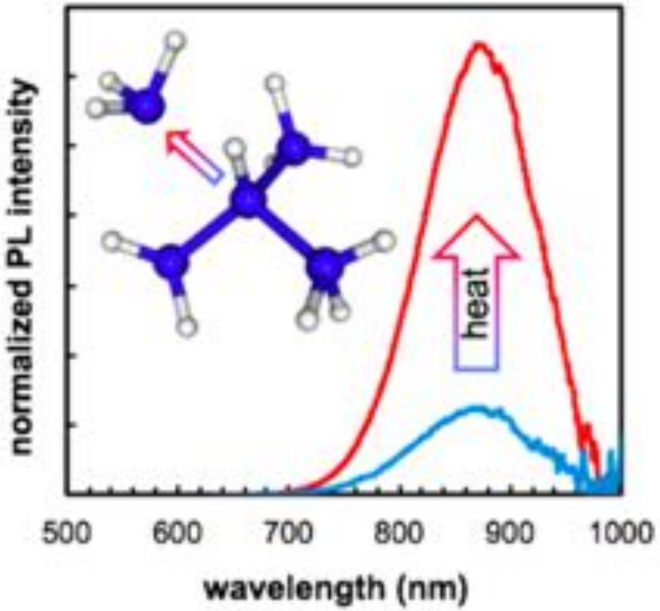


Ligand: 1-octene (C_8H_{16})

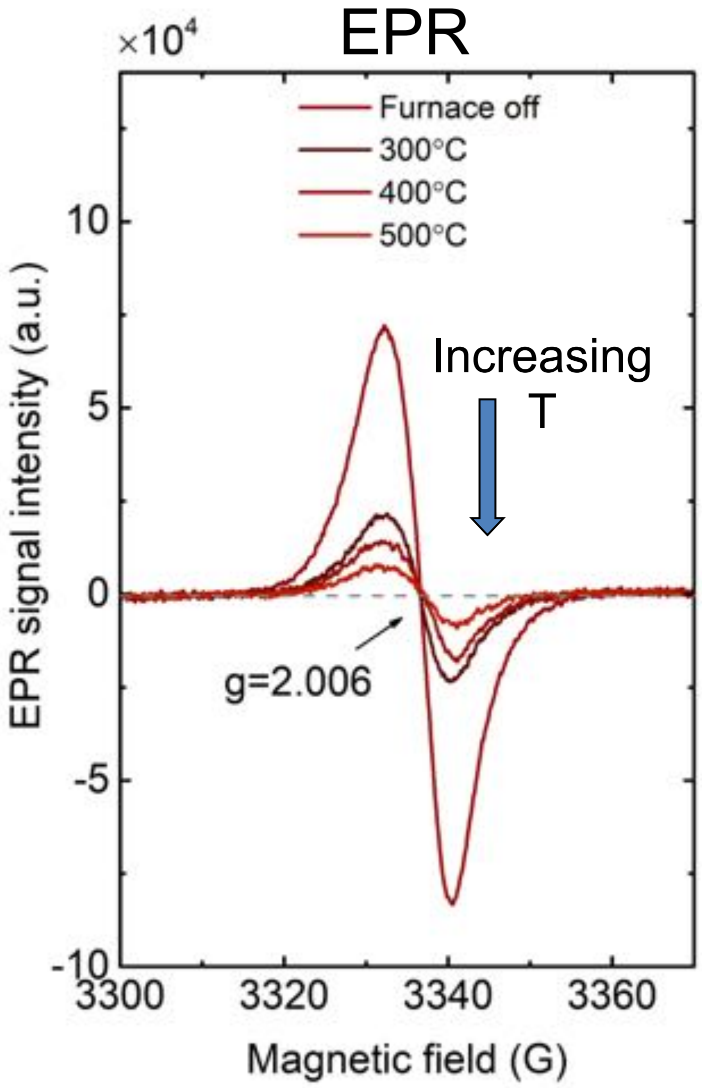


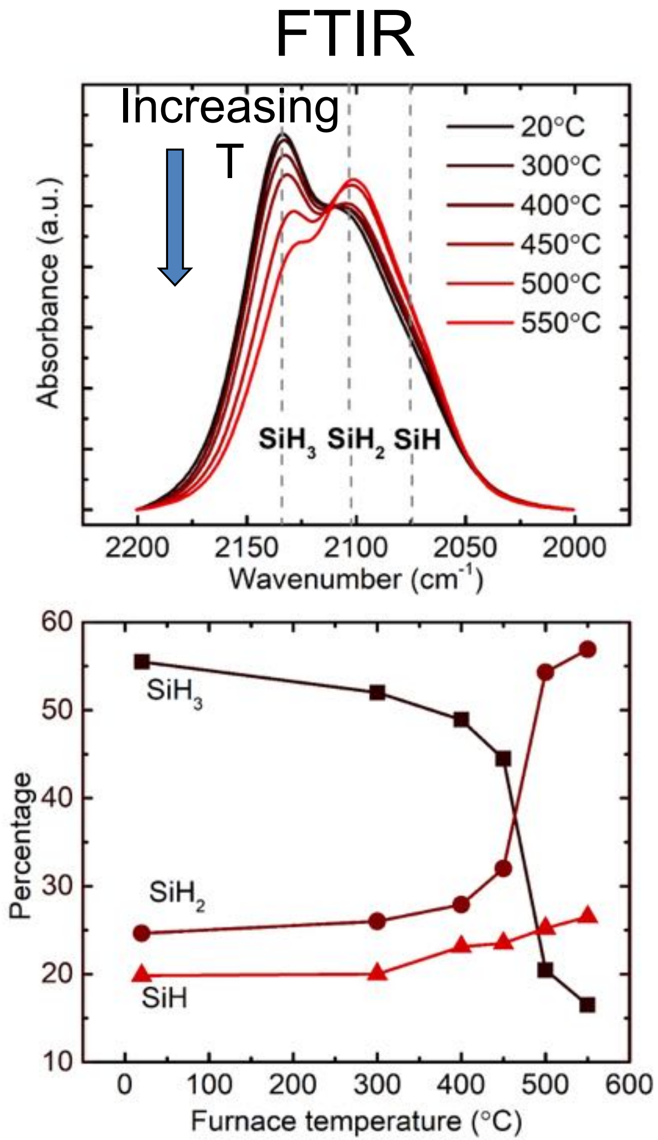
- Furnace heating significantly increases PLQY (Room T to 500ºC)
- Furnace off, PLQY <5%; furnace 500ºC, PLQY ~ 20%

In-Flight Heating Reduces Defects



Shu et al., *J. Phys. Chem. C* (2015)

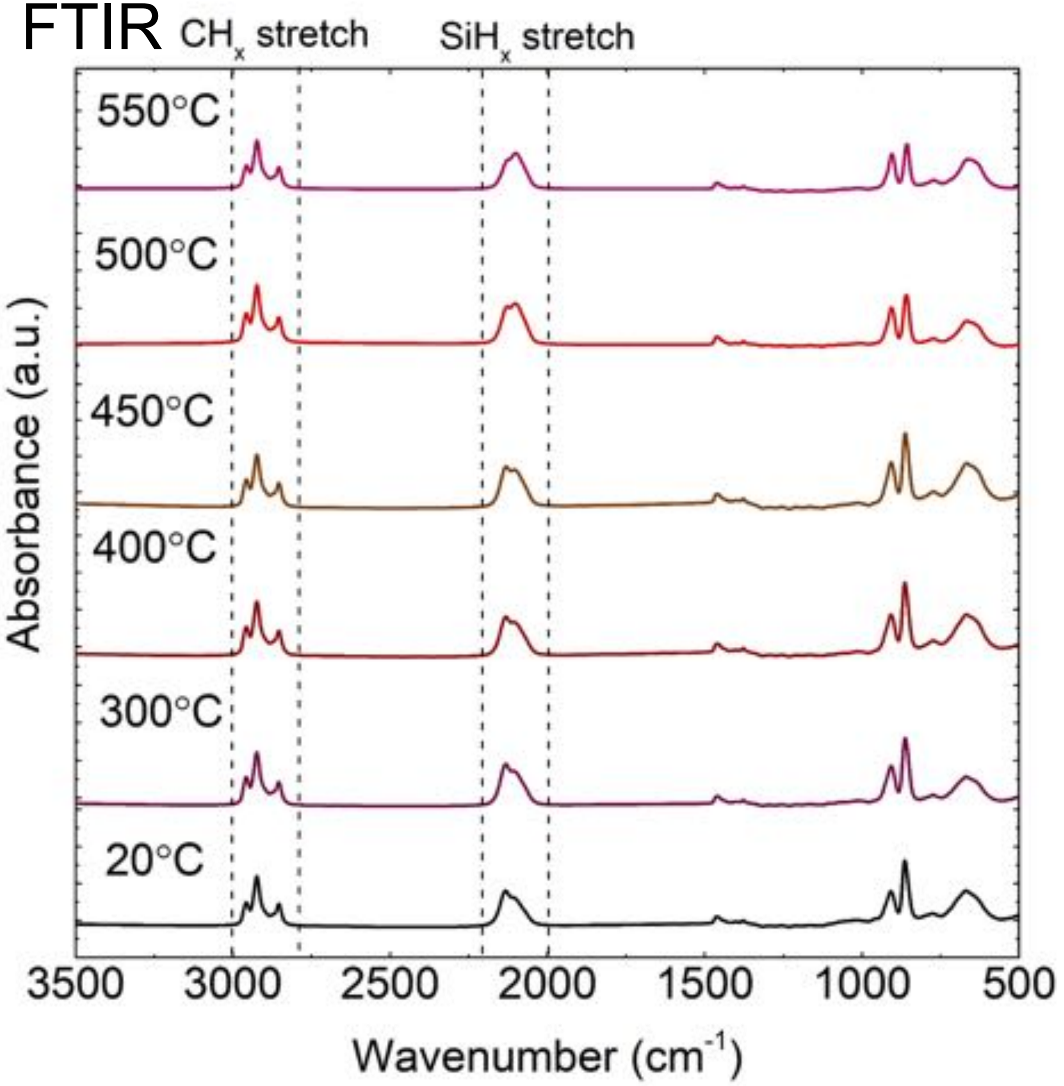


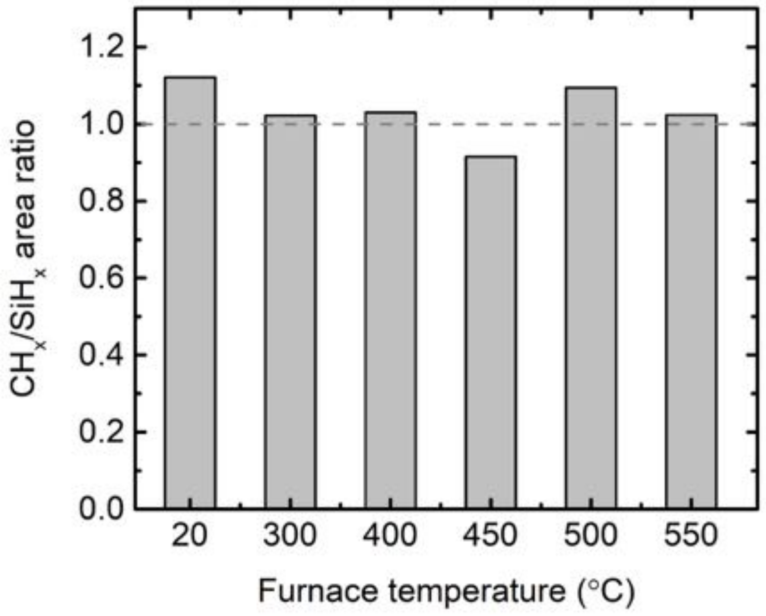


- Heating reduces dangling bond density and weakly bonded SiH_3 species density

In-Flight Heating Does not Change Surface Ligand Coverage

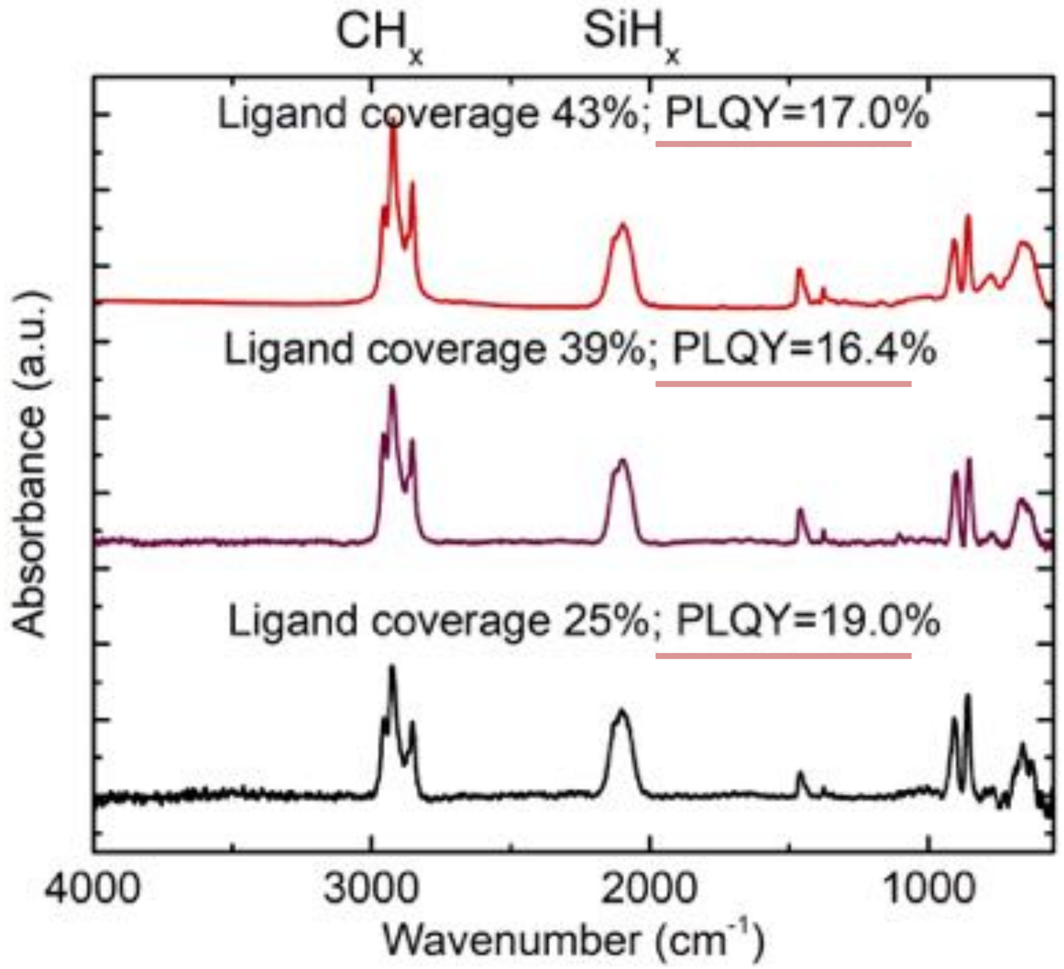
FTIR





- Heating does not increase surface ligand coverage
- Ligand grafting is completed in the plasma

Is PLQY Determined by Surface Ligand Coverage ?



- **Method**: Adjust 1-octene flow rates
- **Conclusion**: Surface ligand coverage has little effect on sample PLQY

  Defects are mostly terminated by hydrogen

Conclusion

- Plasma Synthesis of nanocrystals:
  - monodisperse nanocrystals
  - size control through residence time
  - suitable for high-melting point materials
  - capable of nanocrystal doping
- Plasma produced Si quantum dots may be highly suited for solar luminescent concentrators
- Plasmas may enable all-gas-phase “green” nanomaterials chemistry

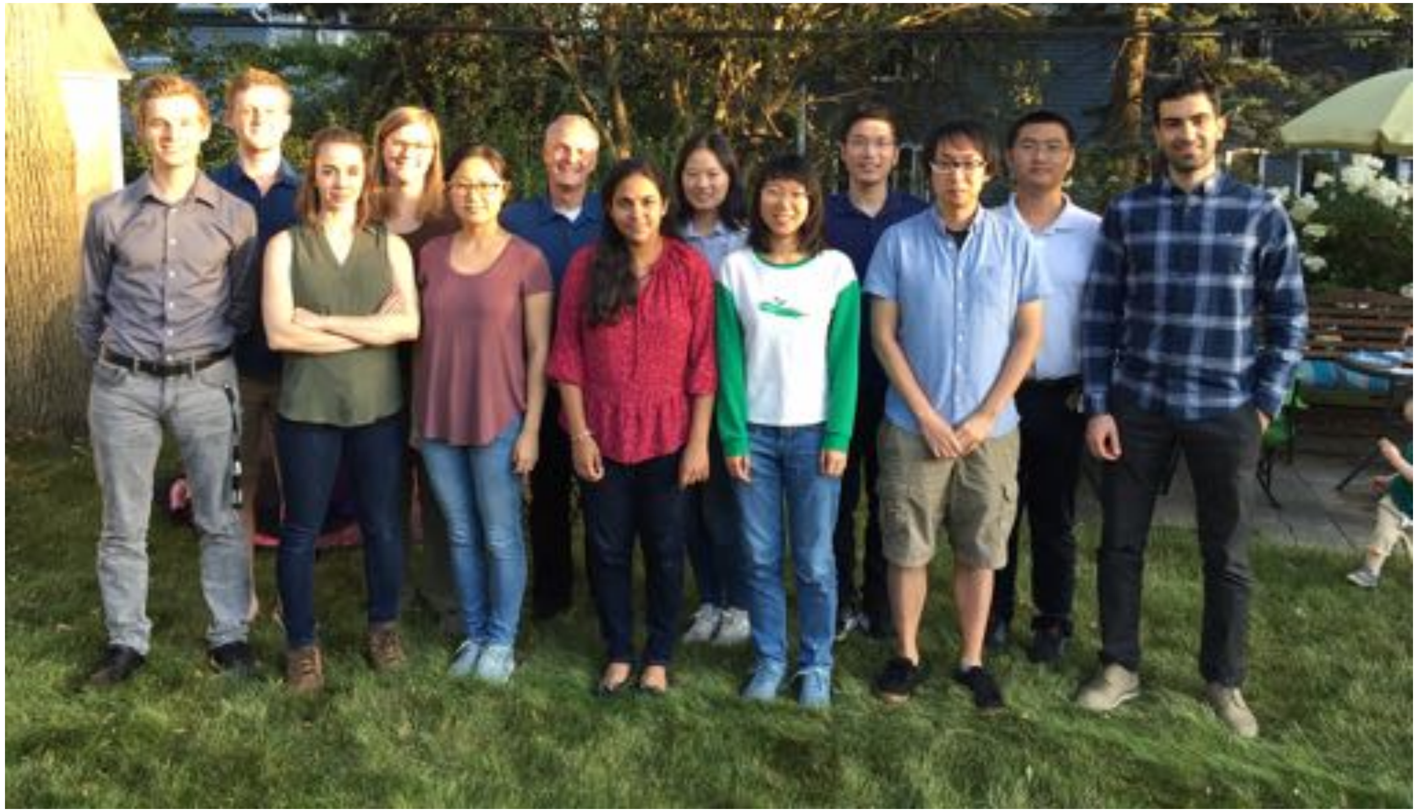
Acknowledgments

NSF

EFRC CASP

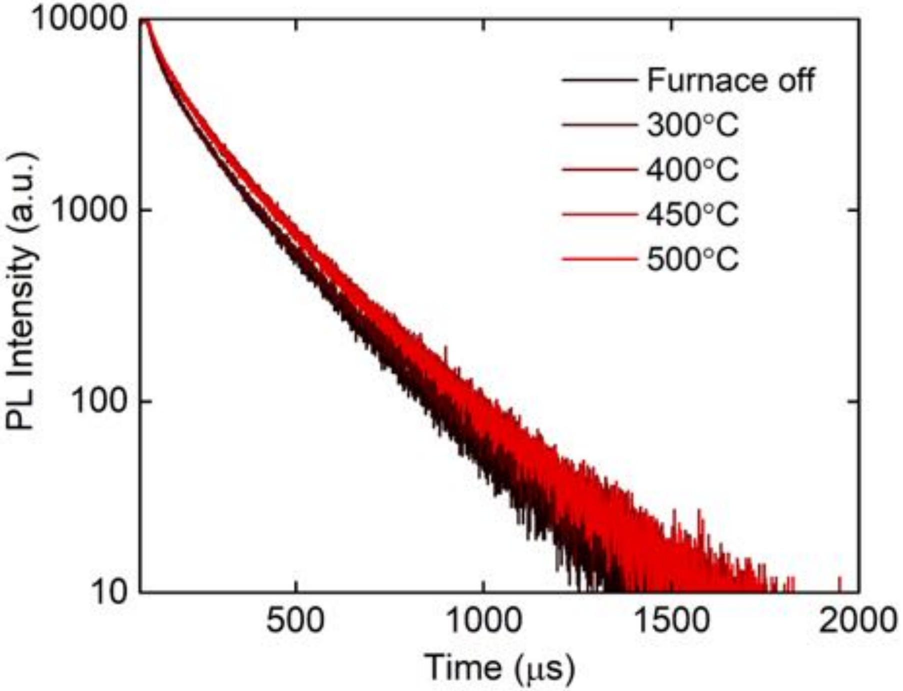
SCIENCE TO SHAPE THE FUTURE OF THE ARMY
ARMY RESEARCH OFFICE
1951

NATIONAL SCIENCE FOUNDATION
MRSEC
NSF
MATERIALS RESEARCH SCIENCE & ENGINEERING CENTERS



In-Flight Heating Reduces "Dark" NC Fraction

$$I = I_0 \exp(-\left(\frac{t}{\tau}\right)^{\beta})$$

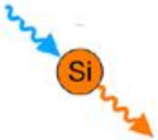


Single NC: Internal quantum efficiency $\mathrm{IQE} = \frac{k_r}{k_r + k_{nr}}$

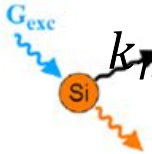
Lifetime $\tau = \frac{1}{k} = \frac{1}{k_r + k_{nr}}$

Ensemble: $\mathrm{PLQY} = \sum \mathrm{IQE}/N$

Sangghaleh et al, ACS Nano, 2015



"Good" Si NC:
Internal quantum efficiency (IQE) = 1;
$\tau = \tau_0 = \frac{1}{k_r}$



k_{nr}

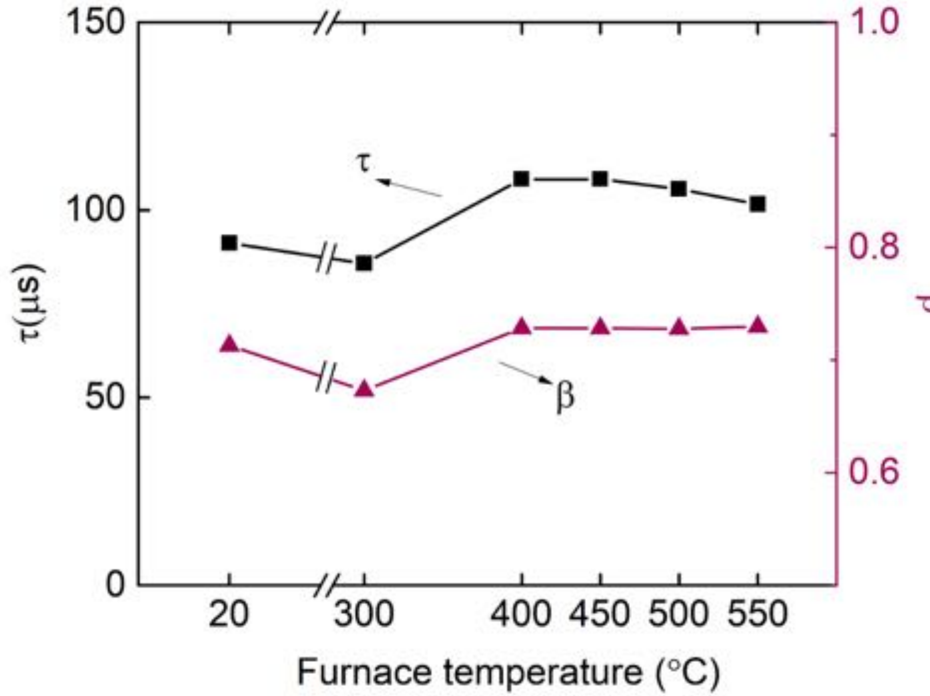
k_r

"Defective" SiNC:
0 < IQE < 1
$\tau < \tau_0$

"Dark" SiNC;
IQE=0

In-Flight Heating Reduces “Dark” NC Fraction

$$I = I_0 \exp(-\left(\frac{t}{\tau}\right)^{\beta})$$



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Sangghaleh et al, ACS Nano (2015)

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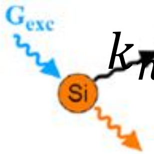


k_{nr}^*

k_r

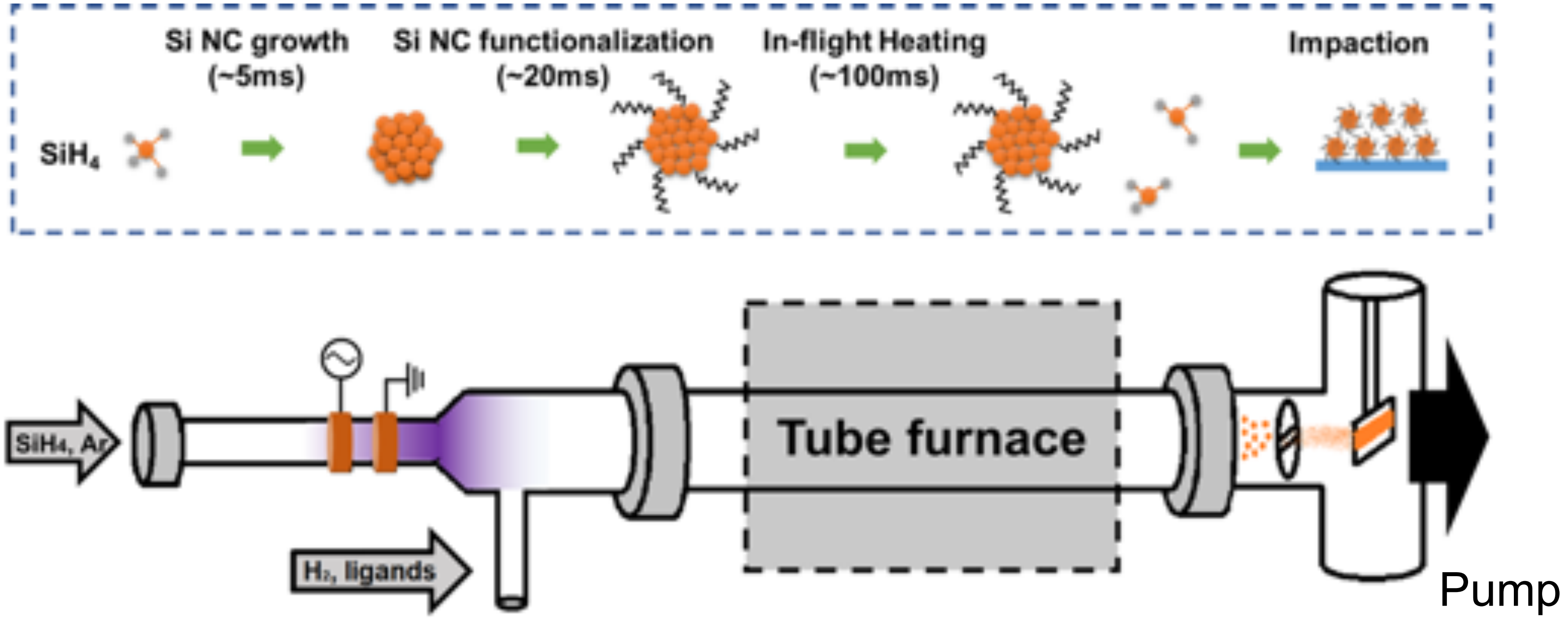
“Defective” SiNC:
0 < IQE < 1

$\tau < \tau_0$

“Dark” SiNC;
IQE=0

- Heating improves the efficiency of each NC ✗
- Heating reduces dark NC fraction

A Platform for Studying Silicon Nanocrystal Properties



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SiH_4/He	14 sccm
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	1-octene
	1-dodecene
	1-octadecene