A Reduction Pathway in the Synthesis of PbSe Nanocrystal Quantum Dots

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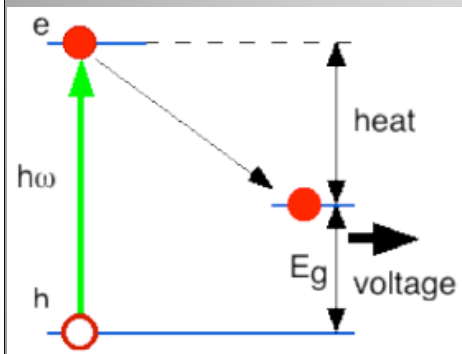
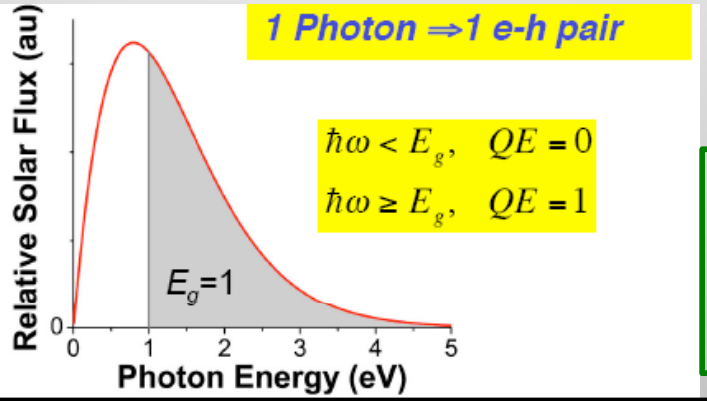
The 7th KOREA-U.S. NANOFORUM

Theoretical limit of solar cells using CM

✓ **Slowered relaxation and cooling (~10X) of photogenerated hot e^- and h^+.**

Traditional solar cell





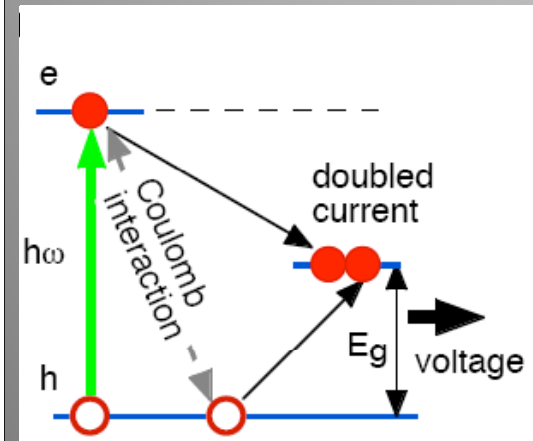
$\hbar\omega < E_g, \quad QE = 0$

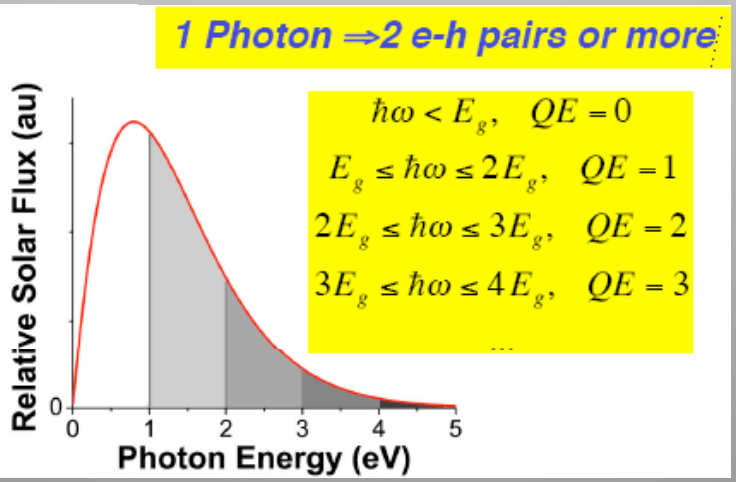
$\hbar\omega \geq E_g, \quad QE = 1$

η_{max} = 31%

W. Shockley and H. J. Queisser *J. Appl. Phys.***1961**, *32*, 510.

Carrier multiplication based solar cell





$\hbar\omega < E_g, \quad QE = 0$

$E_g \leq \hbar\omega \leq 2E_g, \quad QE = 1$

$2E_g \leq \hbar\omega \leq 3E_g, \quad QE = 2$

$3E_g \leq \hbar\omega \leq 4E_g, \quad QE = 3$

...

η_{max} > 60%

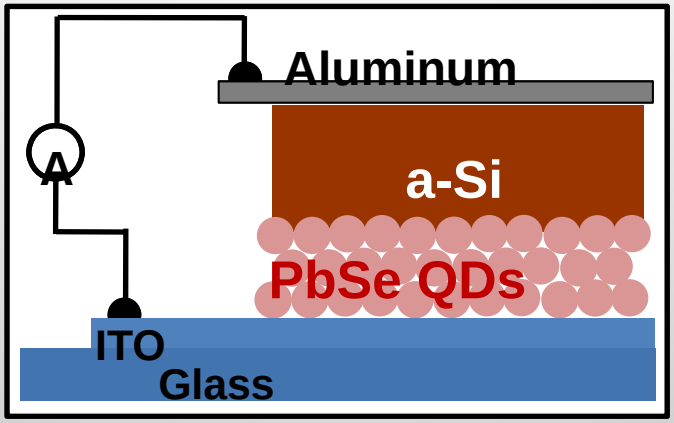
S. Kolodinski, J. H. Werner, H. J. Queisser *Solar En. Mat. & Sol. Cells* **1994**, *33*, 275.

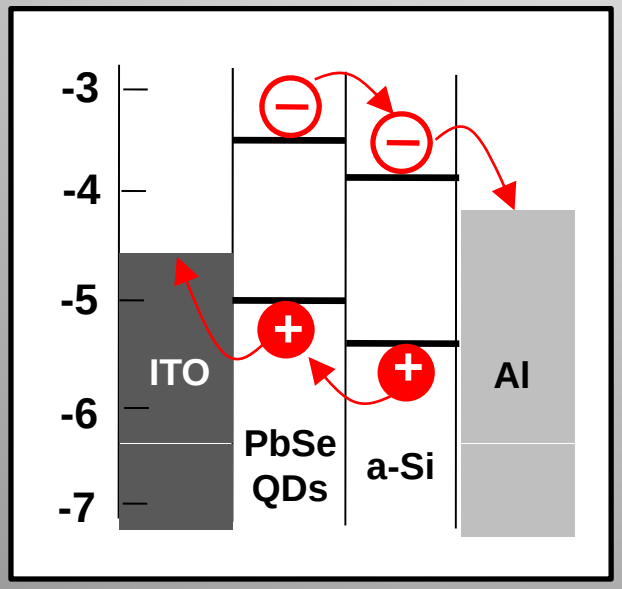
Why PbSe QDs ?

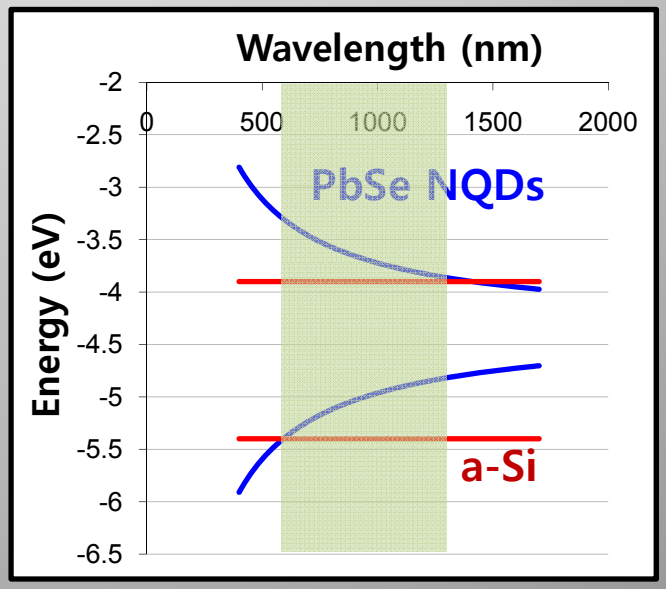
- Band gap energy of 0.26 eV.
- Larger Bohr radius of PbSe compared to other semiconductor.
  - PbSe 23 nm vs. CdSe 1.5 nm
- 8-fold degeneracy at the lowest electronic state.
- Highly efficient Carrier Multiplication (CM).

- ***Preparation methods***
  - **Low production yield ~ 5%.**
  - **Efficiency of CM depends on synthesis prep.**
  - **Hard to control size (too fast growth rate).**

Structure of NQDs solar cell







- ✓ Band edge shift was calculated from effective approximation.

Reduction pathway using HDD

Impurity in TOP ($P(octyl)_3$)

$(R_aCOO)_2Pb + Se{=}TOP \rightarrow [PbSe] + O{=}P(Rb)_3 + (RCO)_2O$: *Too Slow*

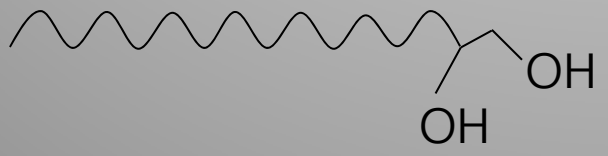
$(RaCOO)_2Pb + PH(R_c)_2 \rightarrow [Pb^0] + O{=}PH(R_c)_2 + (R_aCO)_2O$: *Too fast*

$[Pb^0] + Se{=}P(R_b)_3 \rightarrow [PbSe] + P(R_b)_3$

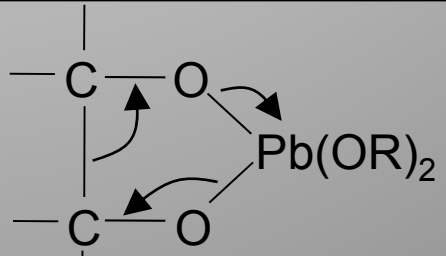
J. S. Steckel et al. *J. Am. Chem. Soc.* **2006**, *128*, 13032.

$(RaCOO)_2Pb + HDD \rightarrow [Pb^0] + HCR(=O) + HCH(=O) + 2R_aCOOH$

$[Pb^0] + Se{=}P(R_b)_3 \rightarrow [PbSe] + P(R_b)_3$

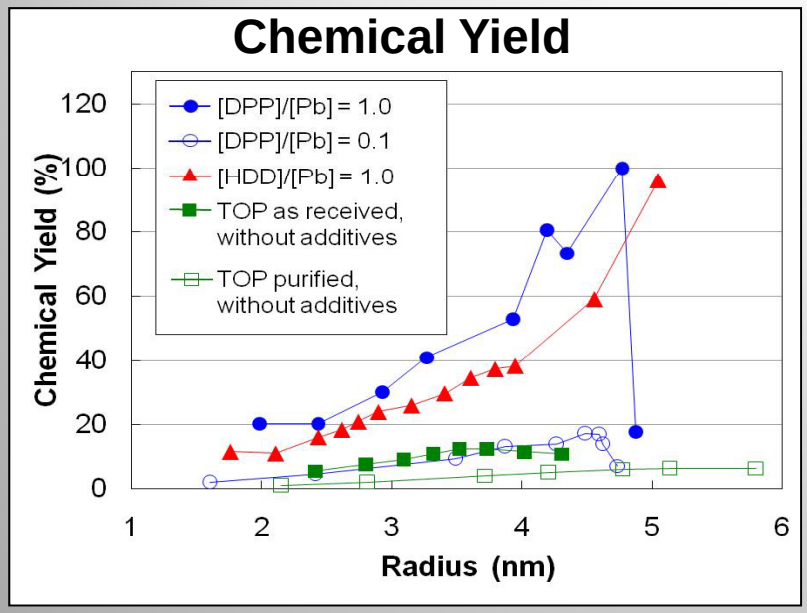


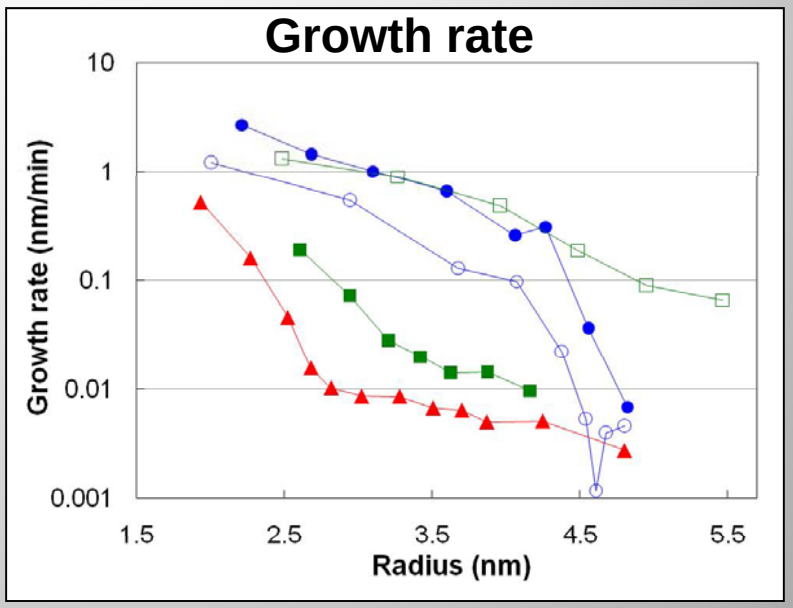
HDD (hexadecanediol)

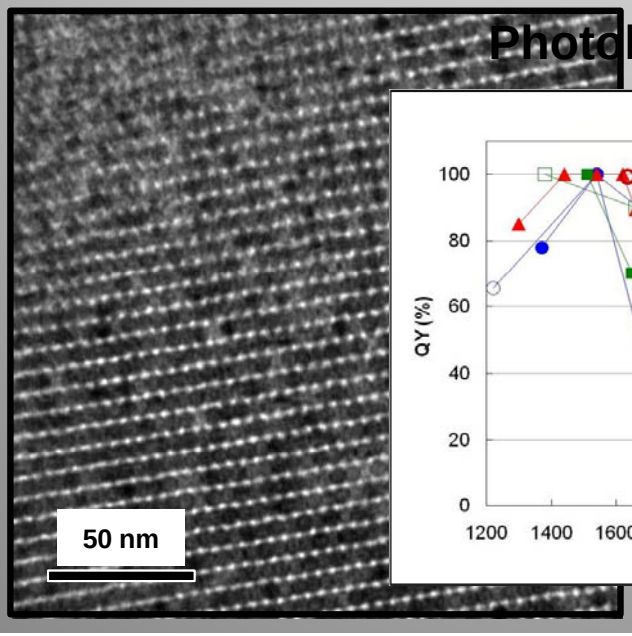


J. Joo et al., J. Am. Chem. Soc., **2009**, *131*, 10620.

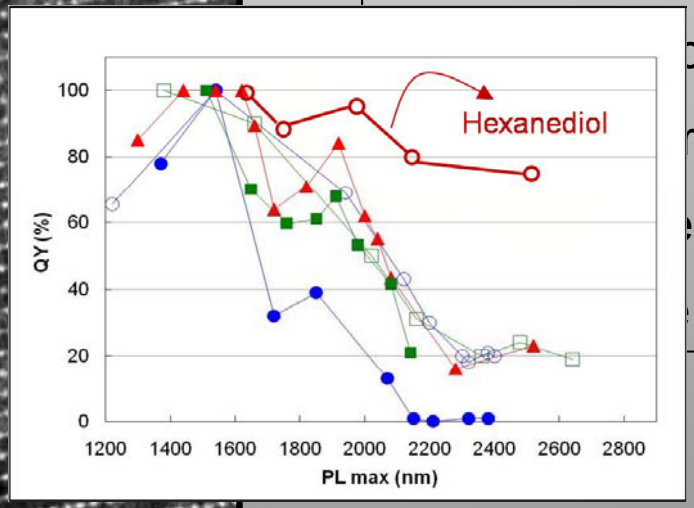
Effect of HDD on PbSe synthesis







Photoluminescence QY



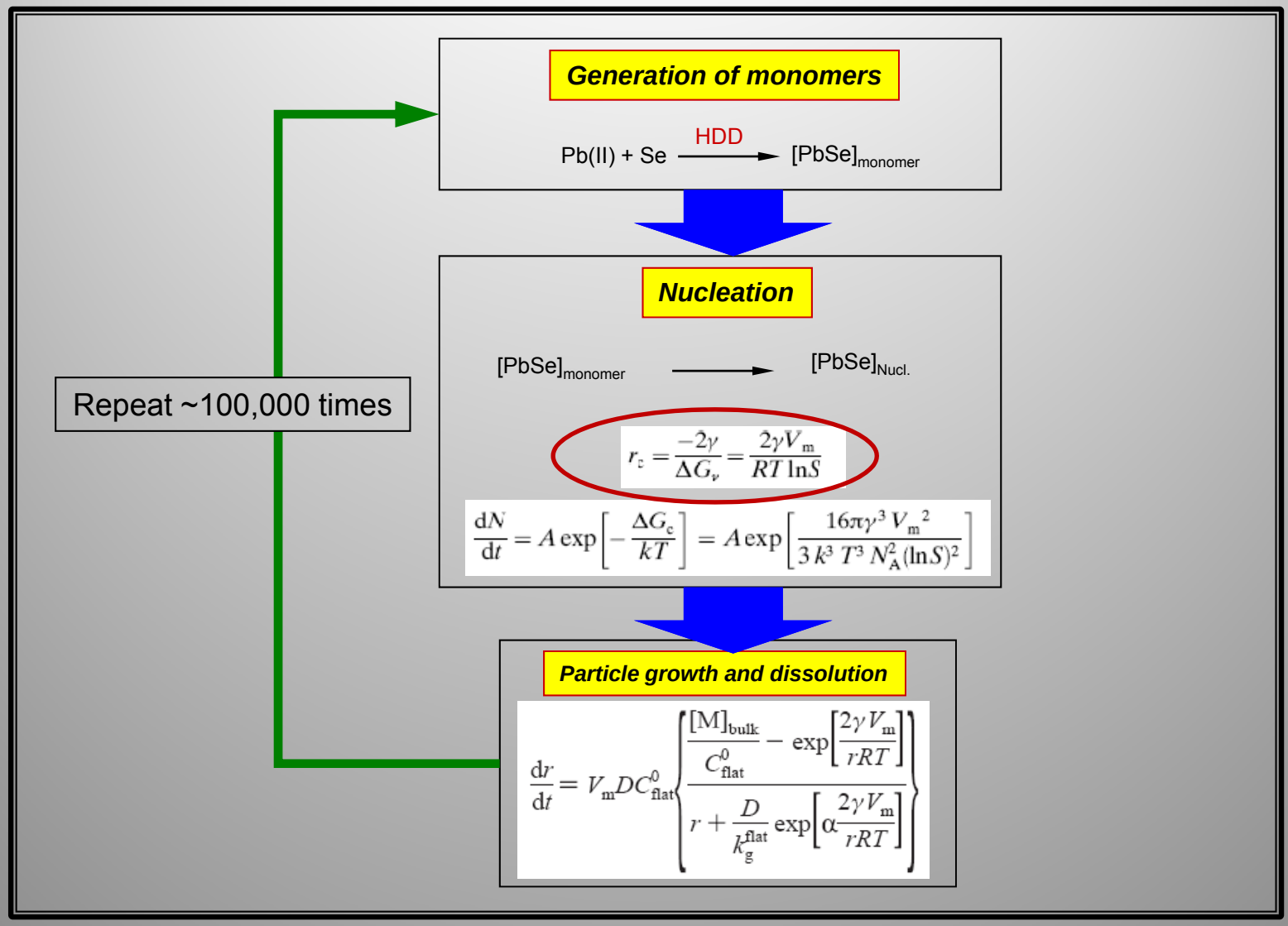
cal yield up to ~ 100%.

ration bigger NQDs.

growth rate.

distribution within 5%

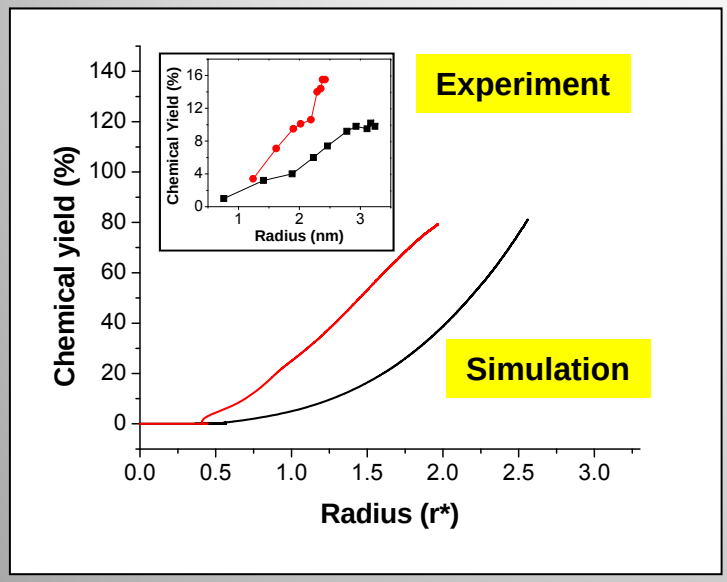
Numerical simulation procedure

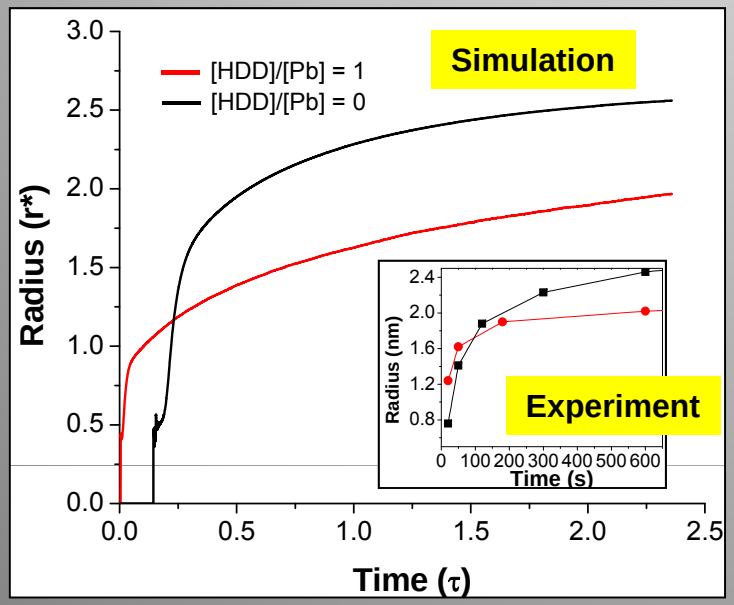


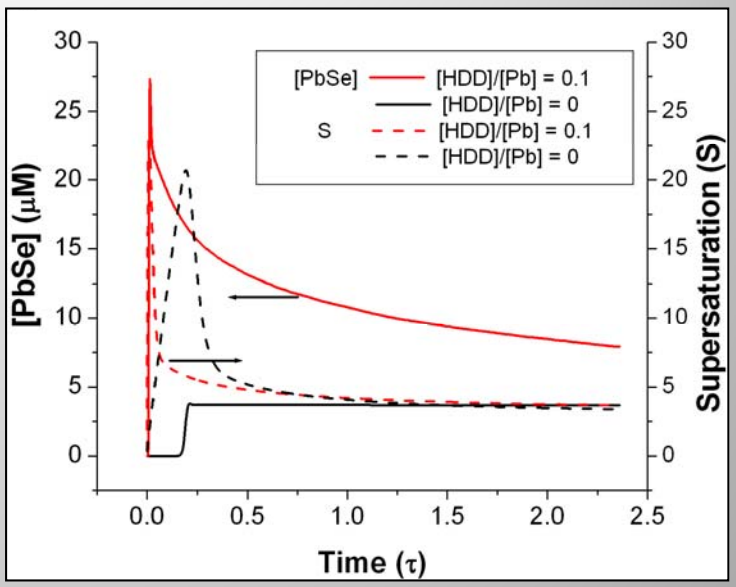
D. V. Talapin et. al. *J. Phys. Chem. B*, **2001**, *105*, 12279.

S.Kwon et. al. *J. Am. Chem. Soc.*, **2007**, *129*, 12571.

HDD effect on QDs growth dynamics







- HDD produces substantial amount of monomer in nucleation step.
- Fast nucleation when HDD was used.
- Sharp nucleation constructs the condition for high chemical yield and QY.

Conclusions

- High chemical yield and precise size control can be achieved by introducing HDD a s a reducing agent.
- High quantum yield can be achieved by using HDD.
- Numerical simulation exactly describes nucleation and growth mechanism of QDs.

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