Watching Nanocrystals Grow:

Real Time, Spectroscopic Monitoring of $NaYF_4$: Yb, Er Upconverting Nanocrystal (UCNC) Synthesis

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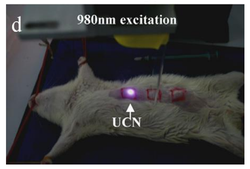
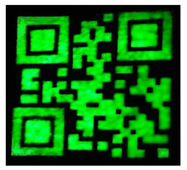
Potential Applications

● Bio-imaging ● Security Printing
● Energy Conversion...



Rat with UCNCs injected below skin under NIR irradiation. Quantum dot luminescence was unable to be seen

D. K. Chatterjee, A. J. Rufaihah and Y. Zhang, Biomaterials , 2008, 29 , 937



Quick response code under NIR irradiation made by UCNC containing inks.

Blumenthal, T, . et. al. Nanotechnology, 23, 2012, 185305 (8pp)

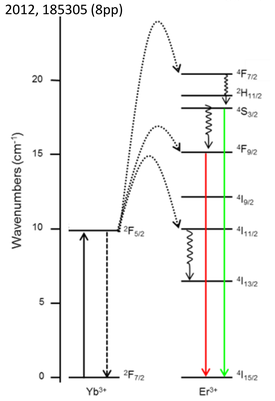
$NaYF_4$:Yb,Er UC Mechanism

Yb^{3+} donor (absorbing species)

- Absorbs 980nm light
- Very long lifetime (~1 ms)
- Can undergo energy transfer with a neighboring Er^{3+}

Er^{3+} acceptor (emitting species)

- Accepts energy from Yb^{3+}
- Additional energy transfer process promotes Er^{3+} into higher energy states
- Results in visible emission from higher energy states



Reaction Procedure[1]

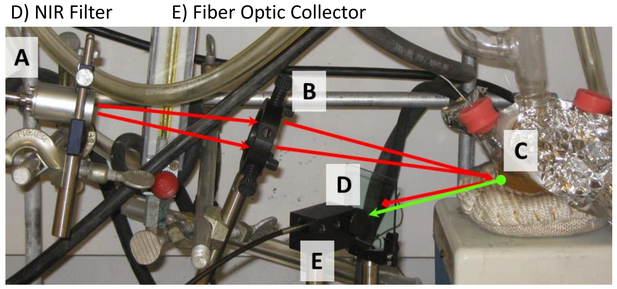
M^{3+}-Oleates: M= Y(80%), Yb(17%) & Er(3%) in Oleic Acid & Octadecene + NaOH NH_4F in MeOH → 1) Remove MeOH 2) Heat under Argon → β-$NaYF_4$: Yb, Er

- Solution was heated to a specific temperature (300-320°C) and held for 1 hr.
- Trying to make β-phase $NaYF_4$ Nanocrystals with diameters <50 nm

1.) H.-S. Qian and Y. Zhang, *Langmuir*, 24, 2008, 12123

Real Time Monitoring Set-Up

A) Laser Head B) Focusing Mirror C) Reaction Flask
D) NIR Filter E) Fiber Optic Collector



Background and Introduction

Initial Results

Crystal Size vs. Reaction temperature

T < 310°C
- Small (< 10nm) UCNCs
- α-phase

T > 310°C
- Very Large (100-250 nm) UCNCs
- β-phase

T = 310°C
- Two results
- Large (30-40 nm) UCNCs
  - β-phase
- Bimodal distribution
- Very small UCNCs
  - Small UCNCs
  - Mix of α-phase and β-phase

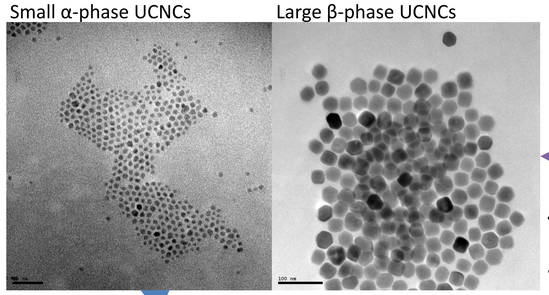
Motivating Questions??

- What is going on at 310°C?
- How can we increase our reproducibility?
- Can we better understand the crystal growth mechanism?

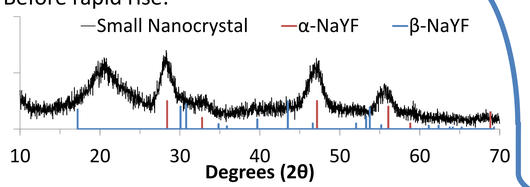
Crystal Analysis

TEM image before rapid rise: Small α-phase UCNCs

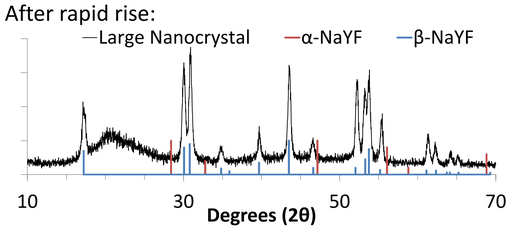
TEM image after rapid rise: Large β-phase UCNCs



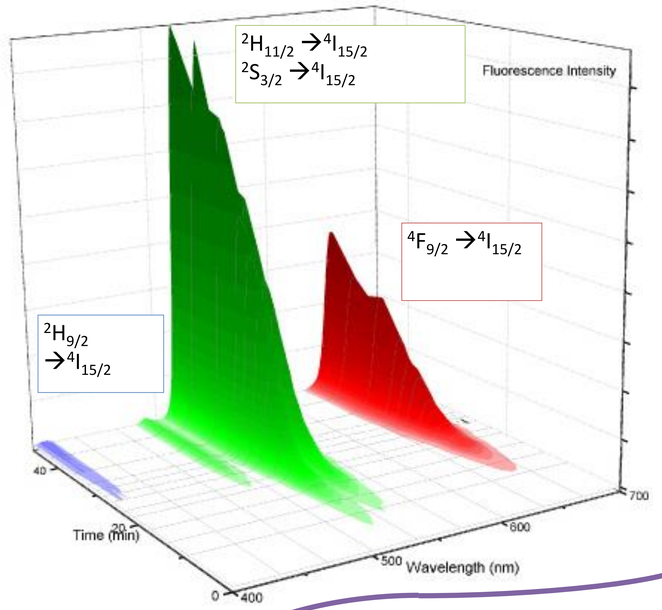
Before rapid rise:

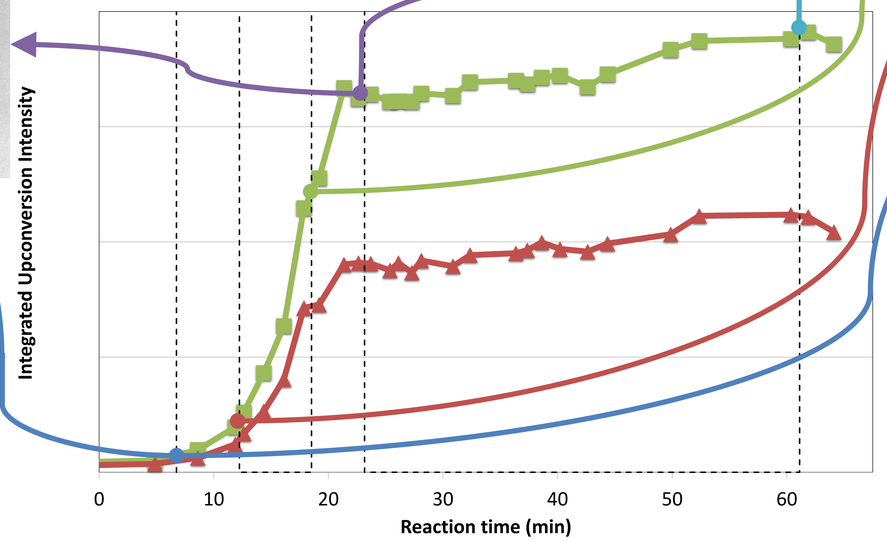


After rapid rise:



Real Time Monitoring



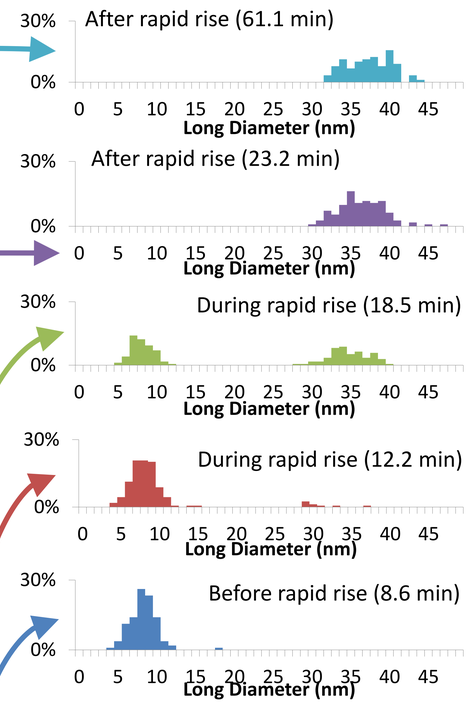


We monitored the UCNC fluorescence from transitions in the green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$), red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) and blue ($^2H_{9/2} \rightarrow {}^4I_{15/2}$) regions. Initially, we observed a very weak fluorescence signal with slowly increasing fluorescence intensity, TEM will later show this to be small alpha phase UCNCs. We then observe a rapid increase in fluorescence intensity over the course of 10-15 minutes.

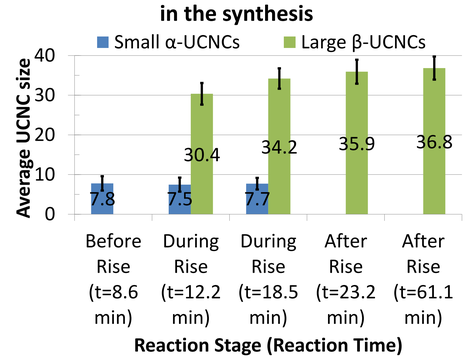
Crystal Size & Size Distribution

Crystal Size vs. Reaction Time

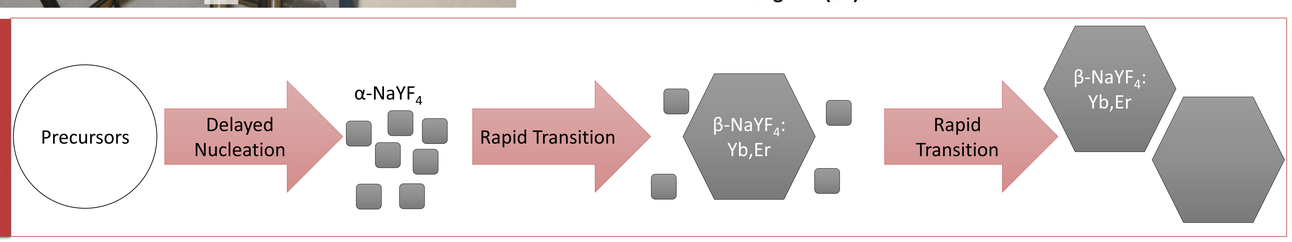
Crystal size and size distributions were measured on samples taken out at various points in the reaction.



Average UCNC size at various points in the synthesis



Proposed Reaction Mechanism



Conclusion

We have shown, that by the real time monitoring the upconversion fluorescence during synthesis a better understanding of the crystal growth process can be obtained. We clearly show the delayed nucleation of small α-phase UCNCs that then undergo a rapid crystal growth and phase change, resulting in large β -phase UCNCs. Furthermore this method has been shown to be a reproducible to make 30-40nm UCNCs with narrow size distributions.

Funding Provided By
NSF: IGERT
NSF EPSCOR