Real-Time Monitoring of Synthesis, Growth Dynamics, and Shell Addition for Upconversion Nanocrystals

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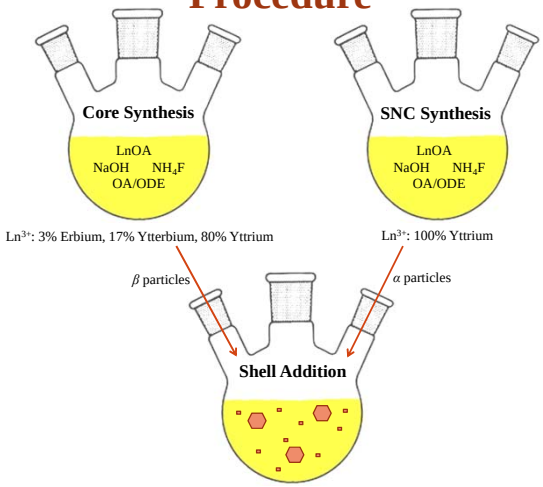
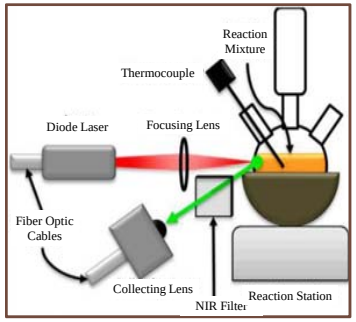
Introduction

$NaYF_4$: 17%Yb, 3% Er upconversion nanocrystals (UCNC) convert near-infrared (NIR) excitation into visible luminescence. These nanocrystals have a wide range of applications, including security printing. To improve emission brightness, a passive shell of $NaYF_4$ can be added to block surface quenching. In this study, real-time monitoring of upconversion luminescence was used to follow the progress of shell additions in 57% oleic acid and 43% oleic acid, respectively. The kinetics and morphological results of the shell addition are presented.

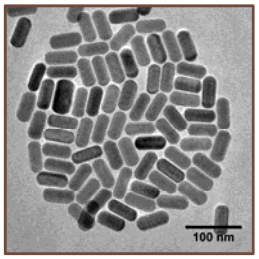
Procedure





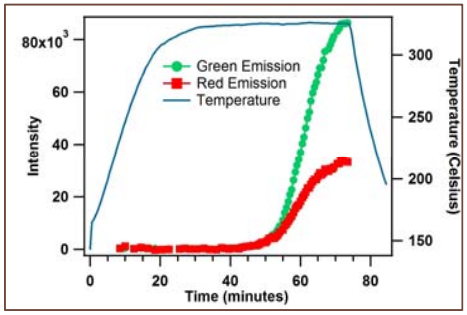
(Left) Real-time monitoring set-up utilized for core synthesis and shell addtion. (Right) Image of luminescence from core-shell-43% near room temperature.

Results

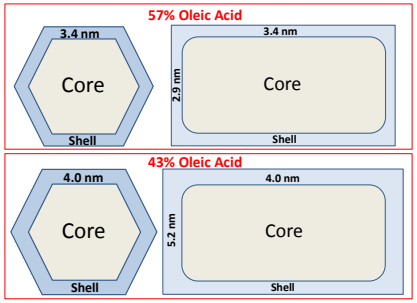


Core UCNC	
[OA]	57%
Length (nm)	56.6 ± 1.7
Width (nm)	26.8 ± 1.3
Aspect Ratio	2.11
SA/V (nm^{-1})	0.153

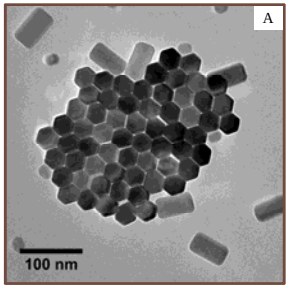
(Left) TEM Image and (Right) statistics for core UCNC.



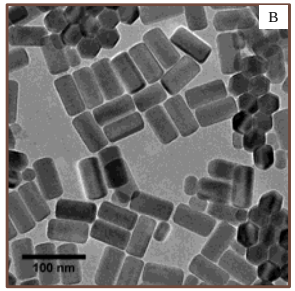
Spectra from real-time monitoring determined completion of core synthesis. Integrated red and green intensities versus reaction time as well as temperature versus reaction time are shown in the graph above. Initiation of heat-up represents time = 0.



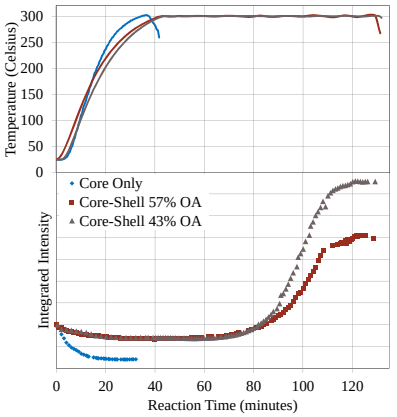
Schematic representation of shell addition in 57% and 43% oleic acid. In 57% OA shell adds preferentially to the ortho-axial faces. In 43% OA shell adds preferentially to the axial faces.



A. TEM of core-shell-57% OA



B. TEM of core-shell-43% OA



Thermal quenching was measured by monitoring the green intensity during heat-up of just core material and compared to the thermal quenching observed during the shell addition. As shown in the graph to the left, thermal quenching was significantly less during shell additions suggesting some passive shell adds during heat up.

Conclusions

- Emission intensity was enhanced through the addition of a passive shell.
- Surface quenching was more greatly reduced in 43% oleic acid, presumably due to the thicker shell.
- Growth was observed more on the ortho-axial plane in 57% oleic acid and more on the axial plane in 43% oleic acid.
- There is evidence shell material adds to the core during the heat-up stage.

Future Work

- Kinetic studies to quantify the surface quenching in the core nanocrystals.
- Evaluate effect of plasmonic surfaces on core versus core-shell upconversion nanocrystals.

Acknowledgments

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