

Polymer Encapsulation and DNA Functionalization of Upconversion Nanoparticles

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I. Abstract

Upconversion nanoparticles exhibit optical properties useful in bioimaging and nano-electronics. The energy upconversion occurs through two-photon absorption of infrared photons and emission of one photon in the visible spectrum. We first encapsulated 16 nm, oleic acid capped β -NaYF₄:Gd/Yb/Er nanoparticles using an amphiphilic polymer. The polymer was prepared by modifying 15% of carboxylic acid groups in poly(acrylic acid) with octylamine. The nanoparticles were then functionalized with single-stranded DNA modified with an amino group. Based on the emission intensity when excited with a 980 nm continuous-wave laser, the encapsulation and functionalization processes decrease emission intensity. Preliminary data on hybridizing the nanoparticle DNA to complementary single-stranded DNA with a rhodamine dye attached show an emission intensity decrease and suggest Förster Resonance Energy Transfer (FRET) between the nanoparticles and the dye.

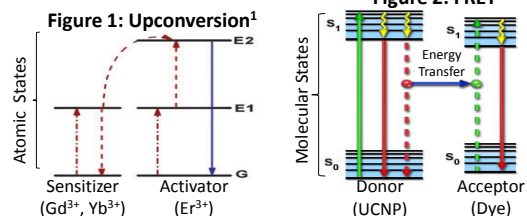
II. Background

•Upconversion Nanoparticles (UCNP)

- Sensitizer ions accept two near-infrared (NIR) photons¹
- Sensitizer donates photons' energy to activator ion¹
- Activator emits one photon in visible range (fig.1)¹
- Modified to be hydrophilic to allow ssDNA attachment^{1,2}
- DNA can be targeted to a complimentary strand²
- Advantages: low cytotoxicity, high signal-to-background ratio, photobleaching resistance, nonmutagenic energy³

•Förster Resonance Energy Transfer (FRET)

- An excited donor particle (UCNP) transfers energy to an acceptor particle (dye on complimentary strand) (fig. 2)⁴
- Acceptor emits 1 lower-energy photon⁴
- Differs from upconversion because it requires one high-energy photon, not 2 low-energy ones⁴

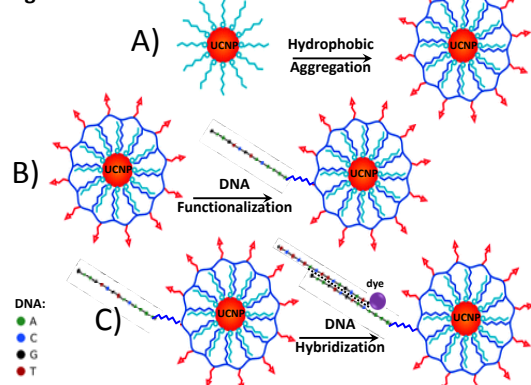


III. Project Objectives

1. Modify β -NaYF₄:Gd/Yb/Er UCNP to be water-dispersible.
2. Attach single-stranded DNA to modified UCNP.
3. Demonstrate FRET between modified UCNP and organic dye.

IV. Methods

Figure 3:

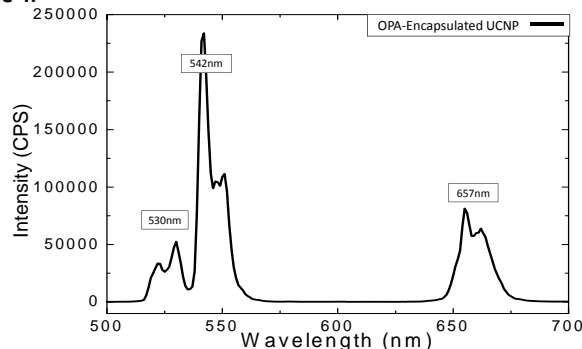


Key: Oleic acid; Octylamine; Remaining carboxyl groups; Carboxy-X-Rhodamine dye

A) Encapsulation¹ of pre-ordered UCNP by adding octylamine-modified poly(acrylic acid) (OPA). B) DNA functionalization at 3' end with amine-modified DNA. Multiple DNA per UCNP. C) DNA hybridization with dye-modified DNA.

V. Results and Discussion

Figure 4:



15% of carboxyl groups on poly(acrylic acid) were converted to amides with octylamine before it was used for encapsulation. The OPA-encapsulated UCNP spectrum shows signature emission peaks at 530 nm, 542 nm, and 657 nm (fig. 4). This data, along with the encapsulated UCNP's easy dispersal in water, shows that encapsulation occurred as desired.

Figure 5:

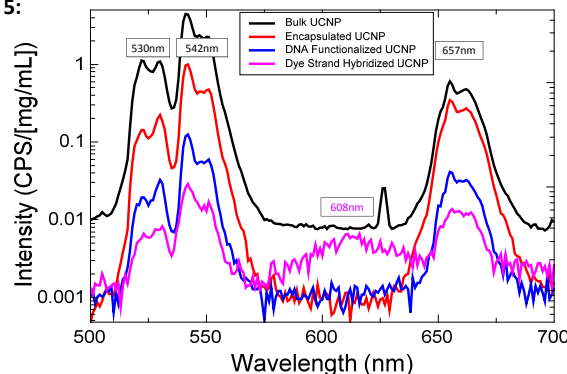


Figure 5 shows emission spectra of bulk UCNP in toluene, OPA-encapsulated UCNP, UCNP functionalized with DNA, and functionalized UCNP hybridized with the dye strand (all normalized by concentration and on a logarithmic scale). Supernatants from purification did not show significant emission; therefore, decreases in intensity are primarily due to quenching.

•Encapsulation causes quenching (fig. 5).

- Water (solvent) is polar and so has high phonon resonance, causing energy loss.²
- Similar quenching found by other groups working with UCNP.²
- Optimization; increased max. intensity of encapsulated UCNP by 4 orders of magnitude.

•DNA functionalization causes quenching (fig. 5).

- DNA is negative, and so could "steal" excitons as water does.⁶
- DNA stabilizes hydrophilicity⁶; more UCNP in supernatant, which do not contribute to final product emission intensity (not technically quenching).

•Dye strand hybridization causes quenching (fig. 5).

- Possible cross-relaxation between dye & UCNP.
- Dye emission peak at 618 nm in preliminary trials suggests weak FRET.
- Could be due to dye strand in solution but unhybridized. Trials in progress.

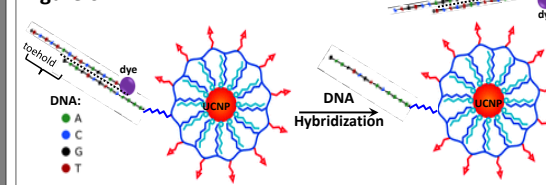
VI. Conclusion

The poly(acrylic acid) modification using octylamine was successful based on FT-IR data. The encapsulation process was achieved and optimized, although there was a large decrease in emission intensity. The functionalization of the UCNP also caused a large decrease in emission intensity. After the DNA was hybridized to the carboxy-X-rhodamine-modified DNA, a small emission peak not present in the UCNP signature spectrum indicates weak FRET between the nanoparticles and dye, thereby providing proof of concept for the DNA targeting system.

VI. Current and Future Work

- Ensure functionalization occurs with a dye on the tether strand.
- More dye strand hybridization trials to show conclusive FRET.
- Dye strand removal with strand invasion⁷ using DNA toehold (fig. 6).

Figure 6:



Key: Oleic acid; Octylamine; Remaining carboxyl groups; Carboxy-X-Rhodamine dye

The removal strand binds to the toehold left unhybridized on the dye strand, then removes the rest of the dye strand.

VII. Acknowledgements

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For more info on upconversion:⁸



VIII. References

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