Synthesis of water-soluble lanthanide-doped upconversion nanoparticles for security printing applications

Prepared by:
Briana Laubacker

Faculty Advisors:
Dr. P. Stanley May
Professor, USD Department of Chemistry

Dr. Qingguo Meng,
Professor, USD Department of Chemistry

Dr. Alfred Boysen
Professor, SDSMT Department of Humanities

Program Information:
National Science Foundation
EEC-1263343

Security Printing and Anti-Counterfeiting REU
Summer 2013

University of South Dakota
414 E Clark Street
Vermillion, SD 57069
# Table of Contents

Abstract .................................................................................................................. 2  

Introduction ............................................................................................................. 3  
- Background ........................................................................................................ 3  
- Objectives ........................................................................................................... 5  

Broader impact ....................................................................................................... 5  

Methods .................................................................................................................. 6  

Materials .................................................................................................................. 6  
Equipment ............................................................................................................... 7  
Experimental Procedure ........................................................................................ 7  
  - Synthesis of lanthanide doped NaYF₄ nanoparticles ................................. 7  
  - Ligand exchange using AEP ........................................................................... 7  
  - Ligand exchange using PAA .......................................................................... 8  
  - Characterization Techniques ....................................................................... 8  

Results and Discussion .......................................................................................... 9  

Conclusion ............................................................................................................. 16  
  - Summary ......................................................................................................... 16  
  - Future Work .................................................................................................. 16  

References ............................................................................................................. 18  

Acknowledgments .................................................................................................. 19
Abstract

Upconverting β-NaYF₄: Yb, Er/Tm nanocrystals are being studied for use in security printing applications. Previous work by our group has focused on using these particles with oleate capping ligands in organic ink formulations. However, to be compatible with the ideal parameters for inkjet printing, nanocrystals dispersible in aqueous-based solvents are required. A ligand-exchange process using the hydrophilic capping agents O-phosphorylethanolamine (AEP) and poly(acrylic acid) (PAA) was performed with the β-NaYF₄: Yb, Er/Tm nanocrystals. The PAA coordinated particles had better stability in both water and a 20% water, 80% ethylene glycol solvent (EG) system than the AEP coordinated particles. With optimization of the PAA ligand-exchange procedure, the PAA capped β-NaYF₄: Yb, Er/Tm nanocrystals will be suitable for use in aqueous ink formulations for inkjet printing of security features.
Introduction

Background

Upconverting nanomaterials have several applications in science, technology, and medicine. Upconversion refers to a process in which a substance undergoes excitation from a light source, and then emits light of a shorter wavelength than the original excitation light\(^6\). This is a useful property for converting near infrared (NIR) wavelengths to visible light, and substances that undergo NIR-to-visible upconversion are especially suitable for use in sensing devices, with applications in the medical field and security printing\(^1,4-7\). Nanomaterials that undergo upconversion are of special interest because their size allows for better integration into composite materials and biological materials\(^7\).

Sodium yttrium fluoride (NaYF\(_4\)) nanoparticles are one example of particles that luminesce under 980 nm excitation when doped with the appropriate lanthanide ions. For example, NaYF\(_4\) doped with Yb, Er or Yb, Tm emit green or blue light, respectively\(^6\). The NIR-to-visible upconversion of these materials is depicted in Figure 1. During upconversion, NIR light is absorbed by the Yb\(^{3+}\) ions, which act as sensitizers. This energy is then transferred from Yb\(^{3+}\) to either Er\(^{3+}\) or Tm\(^{3+}\), depending on which ion the nanoparticles have been doped with, and results in ground-state Yb\(^{3+}\) ions and excited Er\(^{3+}\) or Tm\(^{3+}\) ions\(^4\). Upon subsequent energy transfer, upconversion emission occurs. For materials doped with Er\(^{3+}\), a two-photon process results in green emission. Blue emission from Tm\(^{3+}\) can occur from both a three-photon and a four-photon process\(^6\).
These particles are being studied by our research group for use in security inks. Depending on the capping agent attached to the nanocrystals, the particles can be dispersed in different types of solvent systems. Ink formulations of lanthanide-doped NaYF₄ nanocrystals in organic based solvent systems have been studied. In the work of Blumenthal et al. and Meruga et al., a 90:10 v/v toluene:methyl benzoate solution containing the NaYF₄ nanoparticles and poly(methyl methacrylate) (PMMA) beads was used¹,⁶. However, we are interested in using an aqueous-based solvent system to develop a NIR-to-visible upconverting ink for use in inkjet printing. In the research of Tekin et al., water-soluble CdTe nanocrystals in a poly(vinylalcohol) (PVA) matrix were inkjet printed using a 98% water, 2% ethylene glycol solvent formulation⁸. Various concentrations of nanosized silver colloids were dispersed and printed in a water and diethylene glycol cosolvent system (50 wt. %) in the work of Lee et al.³
Although ink formulations for inkjet printing have been developed using various types of nanomaterials, using lanthanide-doped NaYF₄ nanocrystals has not been widely studied. Previous research using these nanocrystals in security ink formulations has focused on using organic solvents. However, to be compatible with inkjet printers it is ideal to use an aqueous based ink. To address this need, surface modification of oleate-capped NaYF₄: Yb, Er/Tm nanocrystals will be performed in order to disperse them in aqueous systems for use in thermal inkjet printing.

**Objectives**

1. Lanthanide-doped NaYF₄ nanoparticles will be synthesized, and characterized using transmission electron microscopy (TEM) and powder X-ray diffraction (XRD).

2. Ligand exchange using O-phosphorylethanolamine (AEP) and poly(acrylic acid) (PAA) will be carried out so that the particles can be dispersed in aqueous systems for inkjet printing.

3. The luminescence of the particles dispersed in an aqueous system will be studied to determine their effective emission, and whether it remains stable over time.

**Broader Impact**

Counterfeit documents and products have become an increasing problem in recent years, and for this reason the development of more advanced anti-counterfeiting technologies is an important field of study. Security printing using NIR-to-visible upconverting inks is a promising research area, with possible applications in the authentication of money, documents, medicines,
electronics, and other products. With these inks it would be possible to print covert security features on a variety of substances, thereby adding an extra deterrent to counterfeiters.

Upconversion nanocrystals are ideal for use in security inks because they are easily excited by invisible NIR light, and emit in the visible region. NIR-to-visible inks would be more secure than the currently used UV-to-visible downconversion inks, which are easier to obtain\(^1\). Also, the continuous wave laser diodes used for NIR excitation are low-power, inexpensive, and readily available\(^2\). Using these inks for security printing would be more secure because both NIR-to-visible inks and NIR readers are more difficult to duplicate than the currently used UV-to-visible systems\(^6\).

For security printing purposes, NIR-to-visible inks are also suitable because different colors can be printed in the same feature, and observed using the same excitation wavelength\(^2\). For example, quick response (QR) codes using NIR-to-visible upconverting inks have been printed by Meruga et al\(^6\). In this work, different colored upconverting inks were used to add multiple levels of security. This is a good example of how these inks can be used to add extra security features, which cannot be seen under normal lighting conditions and only appear under 980 nm excitation, to important documents or expensive products.

**Methods**

**Materials**

Yttrium (III) acetate tetrahydrate (99.9%), ytterbium (III) acetate hydrate (99.9%), and erbium (III) acetate tetrahydrate (99.9%) were obtained from Alfa Aesar. 1-Octadecene (90%, technical grade) and oleic acid (90%, technical grade) were obtained from Acros Organics and Aldrich, respectively. O-phosphorylethanolamine (AEP, > 98.0%) was obtained from TCI and
polyacrylic acid (PAA, average MW 1,800) was obtained from Aldrich. Chloroform (≥ 99.8%, A.C.S. reagent) was obtained from Sigma Aldrich.

**Equipment**
- X-ray powder diffractometer (powder XRD)
- Transmission electron microscope (TEM)
- Steady state luminescence spectrometer

**Experimental Procedure**

**Synthesis of lanthanide-doped NaYF₄ nanoparticles.** The upconversion nanoparticles were synthesized using the method of Lin et al. In this method, a precursor solution of lanthanide acetates was prepared and then mixed with a fluoride solution. The lanthanide acetates (0.5 mmol) were mixed with oleic acid (6.0 mL) and heated to 100 °C under vacuum for an hour. To prepare the fluoride solution, NaOAc (1.0 mmol) and NaF (2.0 mmol) were dissolved in oleic acid (2.0 mL) and 1-octadecene (10.0 mL). The mixture was reacted at 100 °C under vacuum for 30 minutes, then purged with N₂ gas and heated to reflux (~310 °C). Once reflux was achieved, the precursor solution was injected, resulting in a drop in temperature. Upon recovery of the temperature to 320 °C, the solution was reacted under N₂ gas for another 30 minutes and then allowed to cool. The nanoparticles were precipitated using acetone, isolated by centrifugation, and washed three times with toluene.

**Ligand exchange using AEP.** To facilitate the affinity of the nanoparticles for aqueous systems, a ligand-exchange process using AEP was performed based on the method of Liu et al. First the oleate-capped particles (0.200 g) were dispersed in chloroform (50.0 mL). In a separate flask, AEP (2.0 g) was dissolved in deionized water (60.0 mL), and then ethanol (40.0 mL) was
added to this solution. The two solutions were mixed under magnetic stirring for 10 minutes, and then allowed to separate. Excitation using a 980 nm laser confirmed that the particles were dispersed in the aqueous layer. To collect the nanoparticles, centrifugation of the aqueous phase at 6000 rpm for 10 minutes was performed.

**Ligand exchange using PAA.** To compare with the AEP modified nanocrystals, a ligand-exchange process using PAA was performed based on the procedure of Zhang et al.⁹ A dispersion of the prepared NaYF₄: Yb, Er/Tm particles (0.100 g) in chloroform (10.0 mL) was prepared. This was mixed with a solution of PAA (0.200 g) in ethanol (20.0 mL). The mixture was stirred overnight using a magnetic stir plate. After completion of the reaction, excess solvent was evaporated off and the remaining solution was centrifuged for 30 minutes.

**Characterization Techniques.** To analyze the crystal structure of the synthesized NaYF₄: Yb, Er/Tm particles, powder XRD (Rigaku Ultima IV) was used. The morphology of the particles was determined using TEM (FEI Tecnai G2 Spirit). For spectroscopic characterization of the ligand exchange samples, excitation of upconversion luminescence was excited by a 980 nm continuous-wave (CW) diode laser system (Thor Labs). Emission was collected using a monochromator (Jobin-Yvon, Triax 320) and photomultiplier detector (Hamamatsu, R928). A photon counting method was used to detect the luminescence signal. Igor Pro software was used to analyze luminescence and powder XRD data.
Results and Discussion

Synthesis of NaYF$_4$: Yb, Er/Tm nanoparticles, and characterization via powder XRD and TEM, was performed. For the first NaYF$_4$: 17% Yb, 3% Er sample (BL18Jun13) analysis via powder XRD indicated that the synthesized particles were $\beta$-phase (Figure 2). This phase is ideal, as $\beta$-phase nanocrystals exhibit brighter luminescence. The TEM images of this sample displayed hexagonal, 45-55 nm nanoparticles (Figure 3). Results from TEM of a later sample (BL01Jul13) displayed hexagonal 55-65 nm NaYF$_4$: 17% Yb, 3% Er nanocrystals (Figure 4). The larger particles are preferable for use in security inks because a decreased surface-to-volume ratio results in less solvent quenching and brighter luminescence.

![Figure 2](filename BL18jun13.xrd) Powder X-ray diffraction spectrum of synthesized NaYF$_4$: 17% Yb, 3% Er sample, indicating $\beta$-phase. The top panel represents the BL18Jun13 sample, and the middle and bottom panels represent the references for alpha and beta phase, respectively. The large peak at $2\theta = 39^\circ$ suggests the presence of excess starting material (NaF).
Figure 3. (filename: BL18jun13-0001, BL18Jun13-0007) TEM images of synthesized NaYF$_4$: 17% Yb, 3% Er particles showing hexagonal, 45-55 nm nanocrystals.

Figure 4. (filename: BL01Jul13-0008) TEM image of 55-65 nm NaYF$_4$: 17% Yb, 3% Er nanocrystals.
Ligand exchange using AEP was performed using the BL18Jun13 nanoparticles. After completion of the reaction, a cloudy organic phase and clear aqueous phase were observed (Figure 5). The clear aqueous phase suggested that the nanoparticles successfully coordinated with AEP, and transferred into the aqueous layer. This was confirmed by monitoring the reaction using a 980 nm CW diode laser to detect luminescence in the aqueous phase. During ligand exchange, samples were taken 1, 2, 5, and 10 minutes after stirring from each layer. Results of the emission spectra indicated that the ligand exchange process was completed after 2 minutes of stirring (Figure 6). Although the AEP ligand exchange was initially successful, these particles were not stable in water and precipitated out of solution. Previous work by our group also has suggested that this ligand has a tendency to etch the lanthanide-doped NaYF₄ nanocrystals, which is a likely reason for the observed decrease in stability.

Figure 5. (filename: Expt. 6 - aqueous and organic layers) Aqueous (top) and organic (bottom) phases after AEP ligand exchange. The clear top layer indicates that the nanoparticles successfully dispersed in the aqueous layer.
Due to the instability of the AEP capped nanocrystals, ligand exchange was also performed using PAA. This reaction was performed using NaYF₄: 17% Yb, 3% Er nanocrystals (Figure 7). However, these PAA-coordinated particles were not dispersible in water. This may have resulted from too low a stirring speed during the reaction, which would have allowed the
nanocrystals to aggregate before the ligand exchange was able to occur. The solubility of two of these samples, BL15Jul13 and BL17Jul13, was studied in water and 20% water, 80% ethylene glycol by dispersing the particles (~0.0100 g) in each solvent (5.0 mL). It was observed that both samples formed a cloudy solution in water, but had much better solubility in 20% water, 80% ethylene glycol as this solution was only slightly cloudy (Figure 8).

![Figure 7](filename: 20130601b-0016, 20130619-0022, 20130603a-0032) TEM images of β-NaYF₄: 17% Yb, 3% Er upconverting nanoparticles used for PAA ligand exchange. The nanocrystals (obtained from Dr. Cuikun Lin) pictured here, CL01Jun13b (a), CL19Jun13 (b), and CL03Jun13a (c), are 60-70 nm in size.

![Figure 8](filename: Expt. 18 – BL15Jul13-2, BL17Jul13-2) PAA ligand-exchange samples BL15Jul13 (a) and BL17Jul13 (b) in water and 20% water, 80% ethylene glycol.
Ligand exchange using PAA was also performed using NaYF₄: 25% Yb, 0.3% Tm nanocrystals (obtained from Zack Schulte). After ligand exchange, these particles successfully dispersed in water. The TEM images indicate that some etching may have occurred, as the particles were slightly smaller and less faceted after ligand exchange (Figure 9).

The PAA capped nanocrystals (QM11Sept13, previously prepared by Dr. Meng) were dispersed in both water and 20% water, 80% ethylene glycol. This solvent formulation was chosen because it fits the ideal surface tension and viscosity parameters required for inkjet printing. The emission spectra of the sample dispersed in water displayed an initial decrease in luminescence, which then stabilized after four days, while the luminescence of the sample in 20% water, 80% ethylene glycol remained stable (Figure 10).

Figure 9. (filename: ZMS20Jun13-0016, ZMS062013-PAA-0009) NaYF₄: 25% Yb, 0.3% Tm nanocrystals before (a) and after (b) ligand exchange with PAA.
Figure 10. Emission spectra of PAA capped nanocrystals in water (a) and 20% water, 80% ethylene glycol (b).
Conclusion

Summary

Using $\beta$-NaYF$_4$: Yb, Er/Tm upconverting nanoparticles, ligand exchange was performed with AEP and PAA. Although the ligand exchange process was successful using AEP, the particles coordinated with this ligand had only limited stability in water. Also, past results obtained by our group have suggested that the AEP ligand may etch the nanoparticles. Ligand exchange using PAA resulted in particles with better stability in water. However, complications with the experimental procedure resulted in the PAA ligand exchange only succeeding with one sample of nanocrystals.

A 20% water, 80% ethylene glycol solvent formulation allowed the particles to be dispersed with increased solubility and decreased quenching of emission compared to the nanocrystals in water. This solvent system also fits the ideal parameters of viscosity and surface tension needed for inkjet printing. By optimizing the ligand exchange process to obtain better nanoparticle solubility, $\beta$-NaYF$_4$: Yb, Er/Tm upconverting nanoparticles dispersed in 20% water, 80% ethylene glycol have much potential for use in security inks.

Future Work

Although promising results were obtained with increasing the nanocrystal affinity for aqueous systems, this topic needs to be further investigated. Based on the results of this work, PAA as a capping agent allowed for nanoparticles with bright emission in aqueous systems. However, the exchange process using this ligand needs to be improved to obtain a better success rate. By performing successful PAA ligand exchange, it can be determined whether or not this ligand does etch the NaYF$_4$: Yb, Er/Tm nanoparticles.
Other hydrophilic ligands that may be compatible with the nanocrystals in the 20% water, 80% ethylene glycol solvent system also should be studied. By investigating several hydrophilic ligands, it will be possible to find the optimal capping agent that results in the best solubility and brightest emission of the nanocrystals. It is also crucial that no etching of the nanoparticles is observed, as this would result in decreased emission over time.

It was determined that the ligand-exchanged nanoparticles were dispersible in 20% water 80% ethylene glycol, a suggested solvent system for inkjet printing. Though this formulation has been tested with an inkjet printer, no printing has been done using the lanthanide-doped NaYF$_4$ nanocrystals in this solvent. Once an optimal ligand has been determined, and stability of the nanoparticles in aqueous systems has been confirmed, the nanocrystals should be used in inkjet printing.
References


Acknowledgments

Funding for this research was provided by the National Science Foundation, REU Security Printing and Anti-Counterfeiting Site EEC-1263343. The author acknowledges Dr. P. Stanley May and Dr. Qingguo Meng for advising the research project, and all the faculty and students of the May-Berry research group for advice and support. The author also would like to thank Dr. Alfred Boysen for guidance with the writing process.