Synthesis-driven, structure-dependent optical behavior in phase-tunable NaYF4: Yb, Er-based motifs and associated heterostructures

Haiqing Liu, Jinkyu Han, Coray McBean, Crystal S. Lewis, Prahlad Kumar Routh, Mircea Cotlet, and Stanislaus S. Wong


December 2016

Condensed Matter Physics and Materials Science Department
Brookhaven National Laboratory

U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party’s use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
Synthesis-driven, structure-dependent optical behavior in phase-tunable NaYF₄:Yb, Er-based motifs and associated heterostructures

Haiqing Liu,a Jinkyu Han,b Coray McBean,a Crystal S. Lewis,a Prahlad Kumar Routh,c Mircea Cotlet,d and Stanislaus S. Wong a,b* 

a Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400 
b Condensed Matter of Physics and Materials Sciences Division, Brookhaven National Laboratory, Building 480; Upton, NY 11973 
c Materials Science and Engineering Department, State University of New York at Stony Brook, Stony Brook, NY 11794-2275 
d Center for Functional Nanomaterials, Brookhaven National Laboratory, Building 735; Upton, NY 11973 

*To whom correspondence should be addressed. Phone: 631-632-1703; 631-344-3178 Email: Stanislaus.wong@stonybrook.edu; sswong@bnl.gov

Abstract: Understanding the key parameters necessary for generating uniform Er,Yb co-activated NaYF₄ possessing various selected phases (i.e., cubic or hexagonal) represents an important chemical strategy towards tailoring optical behavior in these systems. Herein, we report on a straightforward hydrothermal synthesis in which the separate effects of reaction temperature, reaction time, and precursor stoichiometry in the absence of any surfactant were independently investigated. Interestingly, the presence and concentration of NH₄OH appear to be the most critical determinant of phase and morphology. For example, with NH₄OH as an additive, we have observed the formation of novel hierarchical nanowire bundles which possess overall lengths of ~5 µm and widths of ~1.5 µm but are composed of constituent component sub-units of long, ultrathin (~5 nm) nanowires. These motifs have yet to be reported as distinctive morphological manifestations of fluoride materials. The optical properties of as-generated structures have also been carefully analyzed. Specifically, we have observed tunable, structure-dependent energy transfer behavior associated with the formation of a unique class of NaYF₄-CdSe quantum dot (QD) heterostructures, incorporating zero-dimensional (0D), one-dimensional (1D), and three-dimensional (3D) NaYF₄ structures. Our results have demonstrated the key roles of the intrinsic morphology-specific physical surface area and porosity as factors in governing the resulting opto-electronic behavior. Specifically, the trend in energy transfer efficiency correlates well with the corresponding QD loading within these heterostructures, thereby implying that the efficiency of FRET appears to be directly affected by the amount of QDs immobilized onto the external surfaces of the underlying fluoride host materials.

Keywords: NaYF₄ nanocrystals, phase control, quantum dots, upconversion, energy transfer
1. Introduction

In recent years, significant attention has been paid to the fabrication of up-conversion (UC) materials due to their potential applications in solar cells, solid-state lasers, optical telecommunications, flat-panel displays, biolabels, and so forth.\textsuperscript{1-3} Radiative relaxation in these systems leads to emission of either visible or ultraviolet light.\textsuperscript{4,5} Amongst many different candidates used as a host lattice, fluoride compounds have been thoroughly explored, owing to their special ability to undergo NIR-to-visible UC emission.\textsuperscript{6} In particular, NaYF\textsubscript{4} compounds denote a material of exceptional interest as a host lattice of UC materials, because they possess inherently lower phonon energies, and can thereby reduce non-radiative phonon relaxation processes with the dopants (such as rare-earth ions) by minimizing interactions between electrons and phonons.\textsuperscript{7-10}

The two most common crystal structures for NaYF\textsubscript{4} are cubic (i.e., $\alpha$-phase) and hexagonal (i.e., $\beta$-phase). In terms of up-conversion efficiencies, the quantum yield (QY) associated with the $\beta$-phase is roughly an order of magnitude higher than that of the corresponding $\alpha$-phase of NaYF\textsubscript{4}.\textsuperscript{11-15} This observation is further substantiated by recent work in which phase transitions from the $\alpha$-phase to the $\beta$-phase and ultimately back to the $\alpha$-phase were controllably induced upon annealing at different temperatures.\textsuperscript{16} Indeed, it was determined that there were distinctive and measurable differences associated with the upconversion luminescence intensity, the spectral intensity distribution, and the luminescence decay kinetics between the $\alpha$-phase and the $\beta$-phase. These results suggested that the hexagonal crystalline structure is in fact a much more favorable host for accommodating rare-earth metal dopants within the NaYF\textsubscript{4} lattice.

Therefore, many previous reports have focused on either (i) synthesizing hexagonal ($\beta$-phase) NaYF\textsubscript{4} meso- and nano-crystals directly or (ii) developing a facile means to convert the cubic $\alpha$-phase of NaYF\textsubscript{4} into its hexagonal counterpart. For instance, Sun \textit{et al.} have reported that
particle morphology and phase transformation were impacted by the reaction time and the choice of ligands.\textsuperscript{17} Moreover, Zhuang et al. have reported on the synthesis of monodisperse spindle-like $\beta$-NaYF$_4$ mesocrystals via an \textit{in situ} ion-exchange transformation from nanorod bundles of Y(OH)$_x$F$_{3-x}$ precursors.\textsuperscript{18} Conversely, Yin et al. have demonstrated that with the proper amount of sodium hydrogen phosphate (Na$_2$HPO$_4$), the crystal structure of NaYF$_4$ can be rapidly transformed from the cubic phase to the hexagonal phase under hydrothermal conditions within as little as 3.5 hours. These as-obtained products are generally monodisperse with diameters of several tens of nanometers.\textsuperscript{19} Similarly, small-sized (~10 nm in diameter), hexagonal-phase NaYF$_4$ can be prepared through the decomposition of CF$_3$COOM (M = Na, Y, Yb, Er, and Tm) precursors at high temperature (300°C).\textsuperscript{15}

In our work, we aim to resolve some of the existing issues in this field. These include (1) the investigation of the experimental parameter space needed to generate the precise (such as 100% of either the $\beta$- or $\alpha$- phases) crystallographic phase of NaYF$_4$ under ambient, surfactantless conditions; (2) a comparison of the relative optical behaviors of the $\alpha$ versus $\beta$ phases of NaYF$_4$, possessing similar sizes; and (3) the control over the morphology of NaYF$_4$ materials with the goal of correlating shape with optical properties.

Therefore, herein, we have systematically investigated the effect of varying reaction variables, such as reaction temperature, reaction time, as well as precursor stoichiometry in the hydrothermal synthesis of NaYF$_4$ nanocrystals in order to examine the critical reaction parameters that determine (or affect) the corresponding phase, size, and morphology of NaYF$_4$. Furthermore, on the basis of such understanding, we aim to deliberately control not only the physical structure but also the chemistry of the resulting family of NaYF$_4$ nanocrystalline motifs via a rational alteration of reaction conditions. That is, our work herein provides for a
comprehensive strategy and a fundamental mechanistic appreciation of ways to provide reproducible and reliable control over the phase, size, and morphology of NaYF₄ simultaneously.

Overall, based upon our cumulative experimental results we report herein, the use of long reaction times, higher temperatures, and increased ammonia concentrations should likely promote formation of the β-phase. In terms of shape and morphology, with increasing reaction time, the shape evolves from small particles (with ~10 nm average diameter) to spherical aggregate structures (with average diameters of 308 ± 11 nm), and finally onto chromosomal-shaped, micron-sized (measuring ~ 2 μm in diameter and 5-8 μm in length) motifs. Moreover, as the reaction temperature was increased from 100 to 220°C, the morphology progressed from small particles (measuring ~150 nm average diameter) to one-dimensional nanorods (with dimensions of ~1 μm in diameter and ~5 μm in length) and ultimately onwards to chromosomal-shaped, micron-sized structures. Finally, when the concentration of ammonia was increased to 0.8 M under relatively mild, ambient synthesis conditions, the morphology consisted of nanowire bundles, with overall dimensions of ~1.5 μm in diameter and ~5 μm in length, composed of constituent, ultrathin (average diameter of ~ 5 nm), micron-long one-dimensional subunits. We should highlight that we are the first to produce and hence observe complex chromosomal-shaped, micron-sized structures pertaining to NaYF₄.

With respect to the intriguing idea of tailoring synthesis to impact upon the intrinsic physical properties of NaYF₄, there has been an interest in the synthesis of NaYF₄-based heterostructures with unique optical behavior.²⁰-²² Indeed, the presence of Förster resonance energy transfer (FRET) observed in such heterostructures could potentially render them as promising candidates for multiplex near-infrared imaging, not only due to the enhancement in the overall signal but also because several defining characteristics of the emission spectra itself,
namely the numbers of peaks observed and their relative intensities, can be readily tuned by altering the excitation wavelength. For example, using FRET, a reversible and stable NIR photoconductivity switch was fabricated using CdSe/NaYF₄ heterostructures that could up-convert NIR photons in NaYF₄ and use the as-generated excitons to create charge carriers within CdSe-based films.

While these prior reports have provided preliminary experimental evidence for the potential of combining NaYF₄ and CdSe quantum dots (QDs) to create novel optically relevant composite structures, a more thorough and systematic study of this issue that transcends the use of either bulk or nanoparticulate-based heterostructures remains lacking. Moreover, we have been further inspired by previous work, incorporating similar classes of materials with unique optical properties as functional components of photovoltaic devices, such as either dye-sensitized solar cells (DSSCs) or quantum dot sensitized solar cells (QDSSCs).

In particular, the inclusion and integration of constituent light-converting materials including both up-converting and down-converting species have provided for a means for improving upon light harvesting efficiency and hence, the resulting solar cell performance. In practice, the presence of UC materials can transform lower-energy photons (> 900 nm) into higher-energy, visible photons (< 750 nm) that are easily absorbed by adjacent, associated light sensitizers, i.e. conjugated organic dye molecules or inorganic quantum dots.

In a preliminary study, Li et al. confirmed the presence of effective energy transfer from NaYF₄: Yb, Tm to CdS, as manifested by the observation of fluorescence decay within the doped fluoride, and have incorporated such heterostructures within a photocatalytic configuration. In terms of DSSCs, recent reports have suggested that increases from 5 to 20% in the overall cell efficiency can be expected in devices incorporating UC materials as compared with ‘dye-only’
As for QDSCCs, an increase in the overall cell efficiency from 3.43 to 4.37% was noted when CdSe QD-NaYF$_4$ hybrid nanostructures had been incorporated into TiO$_2$-based photoanodes. Nevertheless, to improve upon the performance of UC material-based QDSCCs to render them as competitive as analogous DSSCs necessitates a more targeted approach.

Nevertheless, to the best of our knowledge, the fabrication of NaYF$_4$-CdSe heterostructures have focused exclusively on CdSe QD nanoparticles deposited onto NaYF$_4$ nanoparticles, i.e., 0D-0D heterostructures. Therefore, the key point of our study herein is that the morphology of the constituent materials can crucially influence the optical properties of the resulting heterostructures. To highlight the importance of this idea, we cite analogous previous work involving as-prepared LaPO$_4$-CdSe QD heterostructures, wherein we varied the morphology of the LaPO$_4$ constituent from its 1D to its 3D analogue with significant impact upon the degree of energy transfer measured between these two constituent components.

Moreover, other reports associated with the formation of hybrid two-component heterostructures have demonstrated that the morphological characteristics of the energy acceptor species play a significant role in the observed energy transfer process. For instance, Erdem et al. fabricated hybrid composite structures composed of InGaN/GaN multiple quantum wells (MQWs) coupled with conjugated polymer nanoparticles (CPNs) in which energy transfer was found to have occurred from the MQWs to the CPNs. Interestingly, non-radiative energy transfer (NRET) efficiencies were found to be nearly 3-fold higher in MQW-CPN hybrids as compared with analogous hybrid systems in which the polymer constituent consisted of less organized and unfolded chains. Indeed, the morphology-dependent NRET process in that example could be attributed to corresponding alterations in the structural and chemical nature of the interface between the quantum wells and the polymer species. In effect, the observed energy
transfer noticeably varied, depending upon the shape of the attached CPNs, i.e. the energy acceptor. As another example of morphology-dependent energy transfer dynamics, Stevens et al. have shown that in two-component nanoparticles, composed of two distinctive types of fluorene-based amphiphilic polymeric molecules, both the spatial clustering and packing as well as the degree of phase segregation associated with the constituent donor and acceptor molecules within the underlying nanoparticulate matrix collectively had a significant impact upon the overall measured energy transfer efficiencies.33

Therefore, the objectives of our efforts herein are (i) to tune our chemical synthesis protocols to create relatively monodisperse distributions of energy donor species consisting of phase-pure, crystalline, and morphologically well-defined NaYF4 with controllable size and shape and (ii) to incorporate these motifs into CdSe QD-NaYF4 heterostructures in order to modulate their energy transfer behavior. Specifically, we have observed unique and distinctive optoelectronic interactions between CdSe QDs and the underlying NaYF4 upconverting materials within the context of 0D-0D, 0D-1D, and 0D-3D nanocomposites, respectively. In so doing, our results have provided for a more comprehensive understanding of the structure-dependent energy transfer behavior between NaYF4 and CdSe QDs within novel architectures, with implications for the rational design of new classes of photovoltaic devices.

2. Experimental

2.1 Synthesis

Nanoscale motifs (i.e. zero-dimensional (0D) and three-dimensional (3D)) of Er3+, Yb3+ co-doped NaYF4 have been prepared, based on a previously reported hydrothermal approach with a slight modification. Briefly, a total of 0.1 mmol of YCl3, YbCl3, and ErCl3 were weighed
out and dissolved in 10 mL of water. The molar ratio amongst these three metal precursors is 74:18:8. Then, 2 mL of 1 M NaF solution was added in, followed by the addition of 2 mmol of NaCl. Thereafter, a desired amount (i.e. from 0 to 2 mL) of 5 M NH₃·H₂O was added in drop-wise to alter the pH of the final solution. The solution was then vigorously stirred for 15 min, transferred into a Teflon-lined stainless-steel autoclave (with a capacity of 20 mL), and finally sealed. In a systematic series of individual experiments aimed at acquiring mechanistic insights, the autoclave was subsequently oven heated to the desired temperature (i.e. 100°C to 220°C) for a designated amount of reaction time (i.e. 1 hour to 6 hours), and naturally left to cool to room temperature. As-prepared samples were later isolated from solution by centrifugation upon washing with water and ethanol (EtOH), followed by air drying at 80°C overnight.

In order to create a ‘family’ of optically appealing, low-dimensional NaYF₄-CdSe QD based heterostructures, we have also synthesized analogous one-dimensional (1D) NaYF₄ nanorods, based upon a previously reported modification of an existing solvothermal protocol. In a typical preparation, 0.7 g (i.e. 17.5 mmol) of NaOH, 14.2 g (i.e. 45.2 mmol) of oleic acid (90% purity, Sigma-Aldrich), and 10.0 g of ethanol were mixed together to obtain a white viscous solution. 12 ml (i.e. 7.2 mmol) of a 0.58 M NaF solution was added under vigorous stirring, until a translucent solution was obtained. Then 1.5 ml (1.2 mmol) of a 0.80 M ethanolic solution of Y(NO₃)₃ incorporating an optically desirable, optimal Ln³⁺ doping content (18% Yb and 8% Er, molar ratio) was poured into the solution under vigorous stirring. Before transferring to a Teflon-lined autoclave with an internal volume of 23 mL, the solution was aged for 20 min at room temperature. The solvothermal reaction was then conducted in a drying oven at a relatively high temperature of 210°C for a longer reaction period of up to 10 h. After the reaction,
the white products isolated by centrifugation were thoroughly washed with deionized water, and later dried at 60°C for 48 h.

The separate synthesis preparation of CdSe QDs was modified from an existing protocol. Briefly, 0.2 mmol of cadmium oxide (CdO) and 0.8 mmol of stearic acid were added to a three-necked round bottom flask, then de-gassed, and ultimately heated at 150°C under an Ar atmosphere. Once the contents were dissolved, 3.88 g each of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) were combined in a flask and heated to 320°C under an Ar atmosphere. Separately, a precursor selenium (Se) solution was prepared in an air-sensitive glovebox environment, wherein Se was dissolved in tributylphosphine (TBP) and dioctylamine (DOA). Once the solution mixture had reached 320°C within the flask, the Se precursor was subsequently injected, and QD growth was allowed to proceed for 30 mins at 270°C to ensure the production of the desired QD size. After growth was achieved, the solution mixture was later cooled to room temperature, then washed with either methanol (MeOH) or acetone, and ultimately stored in hexane, prior to subsequent processing.

After the synthesis of QDs, 0D and 3D NaYF₄-based heterostructures were formed by mixing 6 mg of the NaYF₄ sample, 6 mL of the CdSe QD solution characterized by an absorption value of 1 a.u., and 0.1 g of oleic acid (OA), respectively, followed by brief sonication and stirring under ambient conditions for 30 mins. The corresponding 1D NaYF₄-CdSe QD heterostructures were synthesized through a slightly modified protocol involving incubation of the mixture of the fluoride, oleic acid, as well as CdSe QD constituent components under an Argon atmosphere, followed by heating to 60°C overnight with stirring.

2.2. Characterization
2.2.1. **X-ray diffraction.** Diffraction patterns were collected using a Rigaku Ultima III diffractometer, operating in the Bragg configuration using Cu Kα radiation (1.54 Å), and scanning a range from 15 to 60°, as measured using a scanning rate of 1° per minute.

2.2.2. **Electron microscopy.** SEM images were collected at 10 kV on a JEOL 7600F instrument. Low-magnification TEM images were taken with an accelerating voltage of 120 kV on a JEOL JEM-1400 instrument, equipped with EDS capabilities. The capacity to obtain high-quality HRTEM images coupled with the ability to obtain reasonable selected area electron diffraction (SAED) patterns were rendered possible using a JEOL JEM-2100F microscope equipped with a Gatan image filter (GIF) spectrometer, operating at an accelerating voltage of 200 kV. Specimens for all of these electron microscopy experiments were prepared by dispersing the as-prepared product in ethanol, sonicking for 2 min to ensure an adequate dispersion of the nanostructures, and finally dipping one drop of the solution onto a Si wafer for SEM and a 300 mesh Cu grid, coated with a lacy carbon film, for TEM and HRTEM analysis.

2.2.3. **FT-IR.** FT-IR analysis was conducted in order to characterize the nature of the external functional groups situated on the surfaces of all of the OA-capped NaYF₄ samples. Specifically, 6 mg of each of the as-prepared NaYF₄ samples was mixed with 0.1 g OA in 6 mL of hexane, sonicated, centrifuged, and oven dried at 90°C overnight. In particular, a Nexus 670 instrument (ThermoNicolet) equipped with a Smart Orbit diamond ATR accessory, a KBr beam splitter, and a DTGS KBr detector was used to collect FT-IR spectra. Data were obtained by placing dried powder samples onto a ZnSe crystal and applying a reproducible pressure. Measurements were performed over the wavelength range of 1000 to 4000 cm⁻¹ using the OMNIC software with a spatial resolution of 4 cm⁻¹ in transmittance mode.
2.2.4. BET analysis. Samples prepared for BET (Brunauer–Emmett–Teller) analysis were initially oven dried to remove any residual solvents. Subsequently, ~100 mg of the as-prepared NaYF₄ sample as well as of the corresponding anatase TiO₂ standard reference material (i.e. surface area of ~10.24 ± 0.54 m² g⁻¹) were each placed within an individual analysis tube, and de-gassed for 2 hours at 220°C to eliminate the presence of any adsorbed species that might have been bound onto the particles’ surfaces. After de-gassing, a BET surface area analysis was conducted using a Quantachrome Nova 2200e Series Instrument through the mediation of a 10-point sampling method.

2.2.5. UV-vis and PL measurement of the CdSe quantum dots. UV-visible spectra of the as-prepared CdSe QDs were collected at high resolution on a Thermospectronics UV1 spectrometer, using quartz cells possessing a 10-mm path length. Photoluminescent data were subsequently obtained at room temperature on a FluoroMax-4 spectrofluorimeter (Jobin Yvon) with a 5 s integration time using an excitation wavelength of 375 nm.

2.2.6. Upconversion Measurements. Upconversion spectra were measured on a home-built Olympus IX 71 inverted microscope equipped with a 100x, 1.4 NA oil immersion objective lens and an Ocean Optics QE65000 multimode fiber optics spectrometer. The excitation source employed was a 980 nm pulse light operating at a 80 MHz repetition rate and a 85 fs pulse width delivered by a Maitai Spectra Physics solid state diode pumped laser which was spectrally separated from the upconverted signal by a dichroic mirror (Semrock short pass 690 nm) and a short pass interference filter (Semrock 700 nm). Upconversion spectra were recorded using an average laser power excitation source of 10 mW focused onto the sample with an integration time of 2 seconds. With regards to NaYF₄, all of the PL spectra herein have already been normalized to their respective sample concentrations. Hence, the observed differences in peak
intensities should reflect the intrinsic properties of the samples tested and prepared under different conditions, which are independent of the actual amount of the sample being tested.

3. Results and Discussion

3.1. Morphological Characterization

To prepare well-defined NaYF₄-based heterostructures in order to properly understand their optical properties, it is critically imperative to correlate the effects of tunable experimental parameters including reaction temperature, reaction time, and concentration of ammonia with the resulting phase and morphology of the constituent NaYF₄ structural motifs. To this end, we have employed a number of techniques including X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques to characterize the as-prepared samples.

3.1.1. Effect of reaction time and temperature

As discussed in the Introduction section, most of the previous reports have utilized high reaction temperatures (i.e. >200°C) coupled with long reaction times (i.e. longer than 10 h) in order to ensure formation of NaYF₄ nanocrystals with a pure β-phase. Herein, we show that similarly chemically pure products can be produced with relatively milder synthetic conditions.

First, we discuss the impact of reaction time. In these sets of experiments, the reaction temperature was fixed at 100°C and ammonia (i.e. standard solution with a concentration of 5 M) was used to adjust the pH of the reaction medium. Herein, the concentration of ammonia was kept constant at 0.2 M. According to the XRD results (Figure S1), the diffraction patterns of all four samples, corresponding to reaction times of 1 h, 2 h, 4 h, and 6 h, respectively, can be indexed to either the pure α-phase (cubic, JCPDS#77-2042) or the pure β-phase (hexagonal,
JCPDS#16-0334) of NaYF₄, or a mixture of both, with no other apparent impurity peaks present. A detailed assignment of the various peaks detected is shown in each panel of Figure S1.

In effect, a longer reaction time appears to promote formation of the β-phase. In fact, as the reaction time increases from 2 h to 6 h, a clear trend was apparent, implying the diminution of the α-phase coupled with the concomitant emergence of the β-phase. In term of morphology, with increasing reaction time, the shape evolves from small particles (with ~10 nm average diameter, Figure 1A) to spherical aggregate structures (with average diameters of 308 ± 11 nm, Figure 1B), and finally onto chromosomally-shaped, micron-sized (measuring ~ 1.9 ± 0.2 µm in diameter and 6.1 ± 1.7 µm in length, Figure 1C and 1D) motifs.

Second, we probe the effect of reaction temperature. In this set of studies, the reaction time was fixed at 2 h, and the concentration of ammonia was set at 0.2 M. According to XRD, not unlike the case with varying reaction times, a higher reaction temperature appears to promote formation of the β-phase (Figure S2). Moreover, as the reaction temperature was increased from 100 to 220°C, the morphology evolved from small particles (measuring 163 ± 23 nm in average diameter) to one-dimensional nanorods (with dimensions of 1.0 ± 0.3 µm in diameter and 4.6 ± 0.8 µm in length) and ultimately onwards to chromosomal-shaped, micron-sized structures, with mixtures of these aforementioned shapes apparent in sample aliquots isolated between these two temperature intervals (Figure 2, panels A through D).

Therefore, with respect to both reaction time and reaction temperature, an increase in either parameter can correspond to an elevated input of thermal energy, thereby favoring the formation of the β-phase, which happens to be the most thermodynamically stable phase, as opposed to the α-phase, an observation consistent with other previous reports. However, our synthetic conditions for the formation of β-phase herein are significantly milder (i.e. lower
reaction temperature and shorter reaction time) as compared with other reports, a reality possibly attributable to the presence of ammonia. Detailed explanations concerning the precise role of ammonia will be discussed later.

3.1.2. Effect of the concentration of NH$_3$·H$_2$O

For these sets of experiments, the reaction temperature was set at 100°C with a reaction time of 2 h, in order to further examine the effect of the addition of ammonia. The reason that we chose these two experimental parameters is that we are expecting a transition from $\alpha$-phase to $\beta$-phase, as we vary ammonia concentration. Hence, we prefer, for our starting point, a set of experimental synthesis conditions that favor the formation of the $\alpha$-phase.

According to the XRD results (Figure S3), the use of a relatively larger concentration of ammonia (i.e. 0.4 M & 0.8 M, respectively), as opposed to comparatively lower concentrations (i.e. 0 M and 0.2 M, respectively), appears to bolster the formation of the $\beta$-phase. Meanwhile, the evolution of morphology is demonstrated in Figure 3. Specifically, when the concentration of ammonia was increased to 0.8 M, the morphology evolved into nanowire bundles, with overall dimensions of 1.5 ± 0.1 $\mu$m in diameter and 5.3 ± 0.6 $\mu$m in length, individually composed of constituent, ultrathin (d ~ 5 nm), micron-long one-dimensional subunits, as shown in Figure 3D.

We emphasize that these specific motifs have rarely if ever been observed with fluorides using similar synthesis approaches. In essence, we believe that the effect of ammonia concentration is superior to that of either reaction time or reaction temperature, as it gives rise to a hexagonal phase even under reaction time (2 h) and reaction temperature (100°C) conditions that appear to largely facilitate the formation of the cubic phase.

3.1.3. Detailed Structure and Crystallinity
We have carefully examined both the representative isotropic (nanospheres) and anisotropic (nanowire bundles) structures we have generated by means of high resolution TEM, as shown in Figure 4. First, depending on the concentration of ammonia used (i.e. 0 versus 0.2 M), the diameters of the spheres may vary from ~150 nm to ~300 nm. The measured $d$-spacing of 0.275 nm can be ascribed to the (200) plane of cubic NaYF$_4$, which is consistent with a standard XRD pattern (i.e. JCPDS #77-2042). Moreover, the SAED pattern can be indexed to the (111), (200), (220), (311), and (422) planes, respectively, of cubic NaYF$_4$, as well. Overall, the electron microscopy results confirmed the nature of the observed crystal structure, which corresponds perfectly well with that of a highly crystalline cubic phase of NaYF$_4$.

On the other hand, we isolated a truly unique and novel morphological motif, i.e. nanowire bundles (synthesized with 0.8 M ammonia), possessing overall lengths of 5.3 ± 0.6 μm and widths of 1.5 ± 0.1 μm, whose crystal structure was consistent with that of a β-phase. We found these nanowire bundles to be composed of constituent component sub-units of long, ultrathin (~5 nm) nanowires with overall lengths of several microns. In this case, the measured $d$-spacing of 0.297 nm can be ascribed to the (110) plane of hexagonal NaYF$_4$, and is consistent with a standard XRD pattern (JCPDS #16-0334). In addition, the SAED pattern can be indexed to the (100), (200), (201), (210), and (112) planes, respectively, of hexagonal NaYF$_4$, as well. In effect, the electron microscopy data substantiated and verified the proposed crystal structure, corresponding perfectly well with that of a highly crystalline hexagonal phase of NaYF$_4$.

The crystalline domain size calculated using the Debye-Scherrer equation can be computed to be roughly 30 nm for all four samples, including those generated using 0 M, 0.2 M, 0.4 M, and 0.8 M ammonia, respectively. However, due to the overall sizes of our as-generated materials, which are close to the micron scale in terms of dimension, such calculations only
provide for an estimate of the crystallite size. We should note that the SAED patterns collected in Figures 4B and 4D imply a clear and distinctive difference in the level of crystallinity between the 0 M and 0.8 M ammonia samples. Such an observation is significant in light of the corresponding optical properties, an issue which will be further discussed in Section 3.2.

3.1.4. Discussion of reaction mechanism

Herein, we have experimentally and independently probed the effects of (1) reaction time, (2) reaction temperature, and (3) ammonia concentration upon the resulting morphology and chemical composition of as-prepared NaYF₄ nanocrystals. As discussed in previous sections, it is not surprising that longer reaction times as well as higher reaction temperatures appear to induce a phase conversion, i.e. from $\alpha$-phase to $\beta$-phase (i.e. moving from left to right in the top schematic of Figure 5) since the $\alpha$-phase is the kinetic product whereas the $\beta$-phase represents the more stable, thermodynamic product.³⁷ In addition, there are many prior reports on this issue, claiming that a minimum of 10-12 h of reaction time as well as reaction temperatures higher than 200°C are necessary in order to generate the $\beta$-phase.¹⁹,⁴⁰,⁴¹

Interestingly, with the use of ammonia, we are able to produce samples with a predominant $\beta$-phase at temperatures as low as 100°C and with reaction times as short as 2 hours. To the best of our knowledge, this desirable reaction parameter space has scarcely been reported, even with similar systems that utilize either hydrothermal or solvothermal synthesis.

Under the present experimental conditions, we observed that ammonia (hydroxide ions) concentration yields two major effects in terms of not only determining crystal structure but also lowering the reaction temperature and time needed to synthesize $\beta$-phase NaYF₄. As we have previously discussed in Section 3.1.2, the formation of all of these structures may be governed by an identical growth mechanism. We have indeed proposed a plausible path of morphological
evolution, summarized in Figure 5, wherein the as-prepared nanowires bundles represent the final achievable end product.

*First,* we observed that the reaction temperature and time needed to synthesize \( \beta \)-phase of NaYF\(_4\) is considerably lower and shorter, respectively, as compared with previous reports. Hypothetically, in the presence of an excess of hydroxide ions in the reaction, Y(OH)\(_3\) can be easily generated as an intermediate species prior to the ion exchange process needed to form NaYF\(_4\), a scenario which can facilitate the formation of hexagonal \( \beta \)-NaYF\(_4\), because as-generated Y(OH)\(_3\) compounds possess the same crystal structure and space group as that of the \( \beta \)-phase of NaYF\(_4\).\(^{18}\) In other words, the presence of Y(OH)\(_3\) due to an excess quantity of hydroxide ions during the synthesis of NaYF\(_4\) can selectively favor the creation and production of the \( \beta \)-phase composition as opposed to the analogous \( \alpha \)-phase one.

A second key finding, consistent with previous reports, is that OH\(^-\) ions can be preferentially absorbed onto the (0001) surface of NaYF\(_4\) and can subsequently inhibit the nucleation and crystal growth along the (0001) orientation in the absence of any ligands/surfactant,\(^{42,43}\) thereby yielding the hexagonal phase of NaYF\(_4\) especially at higher ammonia concentrations. This scenario is consistent with the explanation of the morphological evolution of 1D hexagonal Zn\(_2\)SiO\(_4\) structure in the presence of hydroxide ions.\(^{44}\) Hence, when the concentration of ammonia is higher than the so-called ‘tipping point’ (> 0.4 M ammonia in our case, i.e. pH > 10) within our growth mechanism, growth of the (0001) surface is more significantly hindered. Therefore, under these higher pH conditions, the prospect of isotropic crystal growth (i.e., marked by blue arrows in the bottom schematic in Figure 5), which would have resulted in the formation of \( \alpha \)-phase crystals possessing a spherical morphology, is suppressed. That is, through the controlled adsorption of OH\(^-\), the nuclei of NaYF\(_4\) likely form
with a β-phase composition, and subsequently grow into anisotropic 1D-like motifs (i.e., marked by red arrows in the bottom schematic in Figure 5).

As a separate and corollary issue, we have also observed an inherent morphological preference associated with both phases. Specifically, the α-phase tends to be consistently associated with an isotropic morphology (i.e., small nanoparticles or aggregated spheres), whereas the β-phase is characterized by the presence of anisotropic structures (i.e., chromosomal-shaped motifs in addition to nanowire bundles). We attribute this phenomenon to the inherent crystal structures involved with each of these phases, as has been investigated in previous reports. Specifically, isotropic growth of particles was induced by the presence of cubic NaYF₄ seeds which possess an isotropic unit cell structure, in order to minimize the surface energy of crystal facets. Conversely, the production of anisotropic structures, i.e. either chromosomal or nanowire bundles, is a consequence of selective growth along crystallographically reactive directions (i.e. the c-axis) of hexagonal NaYF₄ seeds, which are associated with the analogous formation of anisotropic unit cell structures.

3.2. Upconversion Properties of NaYF₄ nanostructures

The UC properties of our as-prepared samples have been examined. To probe their intrinsic properties, the UC spectra have been normalized to the amount and concentration of samples analyzed. Significantly, all of the four lanthanide-co-doped NaYF₄ nanostructured samples synthesized under different conditions, specifically with different ammonia concentrations, maintain UC capabilities. Figure 6 depicted the corresponding spectra, where there are basically three emission bands located at 525, 539, and 653 nm, respectively. According to the energy diagram in Figure 6B, the observed peaks correlate with multi-phonon
relaxation behavior from the excited states of $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ to the ground state of $^4\text{I}_{15/2}$, respectively. The peak positions are in agreement with analogous data from literature associated with the UC luminescence of Er and Yb co-activated NaYF$_4$.\textsuperscript{35, 43, 46} As a matter of covering all plausible scenarios, it is also possible that a portion of the incident photon energy may have been dissipated through non-radiative relaxation processes, associated with the $^4\text{I}_{11/2}$ to $^4\text{I}_{13/2}$, $^4\text{F}_{7/2}$ to $^2\text{H}_{11/2}$, and $^4\text{F}_{7/2}$ to $^4\text{S}_{3/2}$ transitions, respectively.\textsuperscript{47, 48}

Amongst these samples, the $\alpha$-phase, characterized by a spherical morphology with average diameters of $\sim$ 150 nm and $\sim$300 nm, that had been prepared both in the absence of ammonia and with 0.2 M ammonia concentrations, respectively, yielded a lower spectral peak intensity as compared with the $\beta$-phase products, the latter of which were typified by either chromosomal or nanowire bundle-shaped motifs which had been generated with either 0.4 M or 0.8 M ammonia concentrations, respectively. These observations are not surprising, since the former two possessed an $\alpha$-phase, whereas the latter two were characterized by a $\beta$-phase, which are intrinsically different in terms of UC efficiency.

The origin behind this observation lies in the differential amounts of non-harmonic phonons within the cubic and hexagonal lattices.\textsuperscript{49} Essentially, the presence of non-harmonic phonons can potentially deter effective energy transfer between the absorption and emission centers.\textsuperscript{50, 51} Specifically, by comparison with the highly-ordered cation distribution within the hexagonal lattice, it has been hypothesized that in the cubic phase, Na\textsuperscript{+} and lanthanide cations randomly substitute with each other in the lattice, thereby leading to the production of additional non-harmonic phonon modes.\textsuperscript{52} Moreover, between the two $\beta$-phase samples, we noted that the chromosomal-shaped sample appeared to give rise to a slightly higher emission intensity as compared with that of the nanowire bundles.
One possible reason for the relatively higher UC luminescence intensity associated with the chromosomal-shaped sample relative to that of the nanowire bundles is that the actual crystalline domain sizes may be different for these two disparate structures. As we have discussed previously, from the X-ray diffraction pattern, these two structures are estimated to possess relatively comparable crystalline domain sizes of around 30 nm.

Data from electron microscopy suggest that the picture is more nuanced. Initially, we hypothesized that the “tip” area may have possessed an inherently different degree of crystallinity as opposed to the “center” area for both the nanowire bundles as well as the chromosomal-shaped samples. As such, we collected TEM images as well as corresponding SAED patterns from both of these two areas within both samples. Interestingly, with respect to the diffraction results, as shown in Figure S5, both the “tip” as well as the “center” of the nanowire bundles (Figures S4A and S4B) are associated with a pattern of ‘diffuse lines’. By contrast, we found a set of ‘sharper, discrete, and isolated points’ for the chromosomal-shaped structures (Figure S4C and S4D). That is, the bundles themselves are actually much more polycrystalline with respect to their analogous chromosomal-shaped samples, which we believe is the reason accounting for their different upconversion results. In general, photoluminescent properties can be significantly affected by both particle size, degree of crystallinity, as well as crystallite domain size. Specifically, the PL intensity typically increases with increasing constituent particle size, crystallite size, and degree of crystallinity. Hence, it would appear that the trend in crystallinity correlates with the corresponding upconversion properties.

3.3. Structure-Dependent Optical Properties of NaYF₄-CdSe QD heterostructures
As an extension of prior studies used to further explore the possible interplay between the NaYF₄ phosphor and other types of light-emitting materials, we have synthesized and characterized a series of NaYF₄-CdSe QD heterostructures, incorporating as-prepared CdSe QDs as well as crystalline NaYF₄ nanocrystals, possessing various types of as-prepared morphologies, i.e., 0D, 1D, and 3D motifs, as described earlier. Specifically, the relevant synthetic protocols for all of the constituent components as well as of the heterostructures are discussed in the Experimental section. We believe the interaction responsible for the formation of the heterostructures does not necessarily involve the creation of a formal bond. Rather, an electrostatic attraction between oleic acid-capped NaYF₄ and hexadecylamine-capped CdSe QDs is likely involved, due to the presence of opposite and complementary charges on the surfaces of these two constituent nanostructures induced by the presence of the different capping agents, according to a previous report.²²

Optical characterization results for as-prepared CdSe QDs have been included in Figure S5. The data imply that the QDs possess a monodisperse size distribution, centered at 5.1 nm.

First, we have characterized the relevant morphologies and chemical compositions of as-prepared heterostructures, utilizing TEM and EDAX spectra, as depicted in Figures 7 and Figure 8, respectively. Based upon the original literature, the average dimensions of the 1D nanorods should be ~100 to 200 nm in diameter with lengths of ~1 µm,³⁵ an assertion corroborated by the corresponding STEM image in Figure 8. Representative TEM images have demonstrated that the CdSe QDs possessing an average diameter of ~5 nm have been successfully attached onto the external surfaces of as-generated NaYF₄ nanocrystals. The corresponding 0D and 3D NaYF₄ depicted in Figure 8 denote samples synthesized under conditions of either 0 M (i.e. nanoparticles with average diameters of ~150 nm) or 0.4 M (i.e. chromosomally-shaped
structures) of ammonia, respectively. Similar elemental mapping images of the heterostructures, implying a uniform and well-dispersed distribution of QDs onto the underlying NaYF₄ motifs, created using either 0.2 M (i.e. nanoparticles with average diameters of ~300 nm) or 0.8 M (i.e. nanowire bundles) of ammonia, were highlighted in Figures S6 and Figure S7, respectively.

We should note, however, that as compared with 0D and 3D NaYF₄-based heterostructures, the extent of QD aggregation is markedly much higher than that noted with their 1D NaYF₄ counterparts. This observation was confirmed in both TEM and EDAX images, a finding which we would prefer to attribute to the prolonged heat treatment (i.e. 60°C overnight) required for the synthesis process of the 1D NaYF₄-CdSe QD heterostructures. Moreover, the relative loading of QDs onto variously prepared NaYF₄, as noted by both EDAX and BET data, is summarized in Table 1.

3.3.1. Role of QD Loading on Energy Transfer and Optical Behavior

Indeed, we have quantitatively analyzed the QD loadings in terms of approximate numbers of CdSe particles immobilized onto certain specific spatial volumes of the underlying NaYF₄ substrates possessing various morphologies. In particular, upon normalization to identical volumes (i.e. 10⁶ nm³) for all of the 0D, 1D, and 3D NaYF₄ structures systematically probed, we noted markedly differential CdSe nanocrystal coverages, ranging from 1000 to over 6000 CdSe QDs deposited onto the fluorides beneath. In fact, these data suggest that the numbers of CdSe QDs are likely to be from 2 to 6 times more prevalent on the outer surfaces of 0D and 3D structures as compared with their 1D nanowire counterparts.

Significantly, with important implications for optical performance, the trend in the physical surface area correlates perfectly well with that of QD loading onto the underlying fluoride motifs. Moreover, we are aware of the additional key nuance associated with the
structural porosity and surface roughness of the NaYF₄ nanoparticulate motifs, as implied by the TEM images in Figure 7B, which account for the higher surface area-to-volume ratios of our larger NaYF₄ motifs. In other words, we have been able to demonstrate that the density of QDs on the surface of NaYF₄ can be readily tuned by simply varying both the morphological and surface area characteristics of our as-prepared nanostructures, the capability of which, to the best of our knowledge, has not previously been reported.

As shown in Figure 9, after the deposition of CdSe QDs, we found that (a) the upconversion signal associated with NaYF₄ has been effectively quenched in all of our heterostructures, coupled with (b) a corresponding increase in the CdSe signal, suggestive of a plausible energy transfer from NaYF₄ to CdSe QDs, as evinced by prior literature. The corresponding energy diagram highlighting all of the relevant excitation, relaxation, and emission processes is shown in Figure 10. Moreover, as depicted in Figure S5, the absorption range of CdSe QDs spans from ~500 to ~650 nm, which overlaps essentially completely with the corresponding emission of the NaYF₄ upconversion materials, thereby further substantiating the plausibility and likelihood of energy transfer occurring between these 2 materials.

We note that QDs serve as a valid reference point and control experiment for better understanding the resulting optical signal enhancement of as-generated CdSe QD-NaYF₄ heterostructures. As such, we find that although the excitation wavelength herein, i.e. 980 nm, is well below the energy of the conventional excitation range of CdSe QDs (i.e. 300-600 nm), the QDs still exhibited a pronounced optical signal upon excitation. Our data are not surprising, since CdSe QDs have been previously shown to give rise to a “two-photon” excitation behavior. Such behavior occurs when the CdSe QDs are excited by two separate photons with
relatively low energy (in this case, 980 nm in wavelength, which is equivalent to 1.26 eV) via a ‘virtual’ energy state located between their ground and excited states.56,57

The extent of the PL signal increase, associated with the CdSe QD peak located at 620 nm, however, is rather different and distinctive for all five as-generated heterostructures. For example, the heterostructures comprising the two differently-sized 0D NaYF\(_4\) samples yielded a greater intensity as compared with the analogous composites, possessing the variously-sized 3D NaYF\(_4\) motifs. This specific finding implies the significance of more available active surface area and porosity, which collectively enable greater QD loading for the 0D-based composites and hence help to account for the observed optical performance.

By contrast, heterostructures incorporating 1D NaYF\(_4\) yielded essentially a negligible change in PL behavior in spite of the ‘reasonable’ surface area associated with the 1D NaYF\(_4\) motifs. To explain this phenomenon, as we noted in the Experimental section, the formation of robust 1D-based heterostructures necessitated a slightly more demanding preparative protocol involving a prolonged heat treatment under an argon atmosphere to ensure the reliable attachment of QDs onto the underlying 1D NaYF\(_4\) nanorods. This experimental reality highlights the crucial importance of the surface chemistry of the constituent NaYF\(_4\) motifs in addition to physical surface area and porosity considerations in the observed QD loading and hence, optical behavior of the resulting heterostructures.

In terms of a more quantitative evaluation of such distinctive, structure-dependent optical behaviors, we have calculated the corresponding energy transfer efficiencies (\(\eta_T\)) with the following expression, Equation 1, assuming that the PL quenching of NaYF\(_4\) can be completely attributed to energy transfer to CdSe QDs:

\[
\eta_T = 1 - \frac{E_S}{E_{SO}}
\]  

(1)
wherein $E_{SO}$ and $E_S$ denote the emission output (i.e., peak area) of NaYF$_4$ before and after CdSe QD attachment, respectively. Herein, we have focused on both the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions (near 525 nm and 545 nm, respectively) as the main peaks upon which to base our calculations, as the upconversion spectra in Figure 9 implied that energy transfer mainly occurs between doped NaYF$_4$ and CdSe QDs at these two specific energy levels.

We should note that our calculations of $\eta_T$ are merely reasonable estimates of the energy transfer efficiencies, since the attenuation of the NaYF$_4$ emission intensity by the presence of the QD itself is not specifically excluded. Hence, the corresponding analysis focuses primarily on determining relevant trends (as opposed to absolute values) in the behavior of the $\eta_T$ parameter. As a consequence, the calculated $\eta_T$ values for heterostructures incorporating 0D and 3D-based NaYF$_4$ synthesized using ammonia concentrations of (a) 0 M, (b) 0.2 M, (c) 0.4 M, and (d) 0.8 M, respectively, as well as of (e) 1D NaYF$_4$ were computed to be (a) 51%, (b) 73%, (c) 48%, (d) 57%, and (e) 27%, in that order. This trend in energy transfer efficiency directly correlates quite well with the corresponding QD loading within these heterostructures (Table 1), thereby implying that the efficiency of FRET is directly impacted and affected by the amount and number of quantum dots immobilized onto the external surfaces of the underlying host materials.

In addition, the green emission versus the red emission intensity ratio (i.e., GRR) data have been extracted from the upconversion spectra of all of the heterostructures involved herein and are depicted in Figure S8. According to the as-obtained results, the GRR values for most of the systems are significantly reduced after the attachment of QDs, thereby further supporting the notion of energy transfer that we have previously proposed. Indeed, we postulate that the energy associated with the green emission is largely transferred to the surfaces of the underlying NaYF$_4$ by the mediating presence of QDs. We do note that the GRR values associated with both the 0.4
M ammonia sample as well as with the 1D NaYF4 sample remain essentially identical after QD attachment. Interestingly, these two samples are also the same ones, incorporating the least amount of QDs amongst all of the five different samples analyzed, according to Table 1. Hence, we have provided further evidence that the physical quantity of QDs immobilized onto the external surfaces of NaYF4 structures can in fact significantly alter the resulting upconversion properties of the NaYF4 host materials.

3.3.2. Role of Surface Chemistry on Energy Transfer and Optical Behavior

To gain insights into the surface chemistry of our NaYF4 nanocrystalline samples, IR spectra were collected and analyzed. As described in the Experimental section, we should note that the IR spectra were taken on oleic acid-capped NaYF4 samples as opposed to bare NaYF4, in order to directly gauge possible peak shifts attributable to the attachment of QDs. As shown in Figure S9 and Figure S10, the peaks at 1390 cm\(^{-1}\), 1463 cm\(^{-1}\), 1560 cm\(^{-1}\), 1720 cm\(^{-1}\), as well as 2850-3000 cm\(^{-1}\) can be assigned to various well-defined and expected vibrational modes, associated with the oleic acid capping agent.\(^{58}\) In the spectrum of as-prepared (ASP) CdSe QDs, characteristic peaks that can be ascribed to P=O stretching (at 1469 cm\(^{-1}\)) as well as C-N stretching (at 1086 cm\(^{-1}\)) modes were present, associated with TOPO and HDA capping agents, respectively. As expected, in general, all of our CdSe QD - NaYF4 heterostructures possessed peaks associated with both of these two constituent component species.

Interestingly, unlike either the 3D or 1D systems (Figure S10), we noted that all of the 0D NaYF4 and corresponding heterostructured samples were characterized by a broad peak situated at 3300-3500 cm\(^{-1}\) (Figure S9), suggestive of an O-H stretching mode associated with hydrogen bonding. It is unlikely that an O-H stretching peak located at such a high wavenumber (> 3400 cm\(^{-1}\))
cm$^{-1}$) can be ascribed to oleic acid alone.\textsuperscript{59} On the other hand, prior work suggests that OH functional groups may exist on the surfaces of NaYF\textsubscript{4} nanocrystals that had been fabricated in either an aqueous or water-containing environment.\textsuperscript{52, 60, 61} In addition, after formation of the 0D-based heterostructures, the OH stretching peak position appeared to have shifted to higher wavenumbers. According to a previous study of analogous CdSe QD-CaWO\textsubscript{4} heterostructures, such a shift in the O-H stretching peak mode may be indicative of a hydrogen bonding interaction between the H atoms and the P=O moiety within residual TOPO capping agents coating the CdSe QDs.\textsuperscript{62} We thereby hypothesize that the presence of these hydroxyl groups located on the external surfaces of our 0D NaYF\textsubscript{4} motifs may have served as “anchoring” sites for the subsequent attachment of CdSe QDs, and that these groups could have thereby facilitated and assisted in QD immobilization in creating the desired heterostructures.\textsuperscript{63-65}

Nevertheless, it is clear that regardless of the precise role of hydroxyl ‘anchoring sites’, it is likely a less important effect. In fact, the primary determinant for QD loading onto the resulting heterostructures is the corresponding surface areas of the various 0D, 1D, and 3D NaYF\textsubscript{4} motifs (Table 1), as there is a direct and significant correlation between these two parameters. In this light, it is not surprising that a more rigorous and prolonged heat treatment was required to generate 1D NaYF\textsubscript{4}-based heterostructures, as our data show that 1D NaYF\textsubscript{4} nanowires possess neither surface hydroxyl groups nor a large active surface area for reaction.

Therefore, it is likely that a fortuitous combination of available morphology-driven physical surface area coupled with beneficial surface chemistry served to increase the amount of CdSe QD loading onto the underlying 0D and 3D NaYF\textsubscript{4} nanostructures as compared with their 1D NaYF\textsubscript{4} analogues. This synergistic effect yielded noticeably greater energy transfer efficiencies for these 0D and 3D-based motifs as compared with their 1D counterparts. Moreover,
increased QD loading and porosity in particular primarily accounted for the overall superior performance of the 0D NaYF₄-based heterostructures as compared with their 3D analogues.

4. Conclusions

We have highlighted herein the ability to control the size, shape, morphology, and phase of NaYF₄. Of particular significance, we are the first to reproducibly produce and hence observe complex chromosomal-shaped, micron-sized structures pertaining to NaYF₄ as a unique motif.

In the process, we have demonstrated structure-optical property correlations within heterostructures incorporating chemically pure, crystalline, phase-defined, and morphologically distinctive fluoride motifs. As an initial set of experiments, in this report, we have synthesized both cubic (α-) and hexagonal (β-) phases of NaYF₄ nanocrystals using a facile hydrothermal synthetic approach. Specifically, we have deliberately isolated samples with an exclusive crystalline phase, possessing distinctive morphologies in the absence of surfactant, merely by carefully varying reaction parameters, including reaction temperature, reaction time, and the concentration of added ammonium hydroxide. According to our results, the alteration of these reaction conditions affects not only the shape but also the phase of as-generated NaYF₄ nanocrystals. For instance, under our relevant reaction conditions, the β-phase could be readily produced with longer reaction times and higher reaction temperatures. The critical inflection point is associated with reaction conditions of 2 hours and 140°C, respectively.

Moreover, most importantly, by changing the concentration of ammonia used, the growth mechanism can be readily controlled. In other words, spherical aggregates of the α-phase can often be readily formed at low ammonia concentrations, whereas bundles of nanowires of the β-phase, composed of constituent ultrathin wires, are frequently isolated at high ammonia
concentrations. In terms of optical properties, we have been focusing on the effects of both phase and shape, and we have confirmed that the presence of the β-phase as well as of the larger overall crystalline domain sizes can lead to the measurement of improved UC efficiencies.

Furthermore, we have probed the fundamental structure-dependent energy transfer behavior of NaYF₄-CdSe QD heterostructures. Specifically, we have demonstrated that the nanoporous 0D particles, characterized by a relatively higher surface area coupled with surface “anchoring” hydroxyl groups for optimal QD loading, could serve as an energy donating species towards CdSe QDs. We believe that our studies associated with the synthesis of a family of morphology-driven CdSe-NaYF₄ heterostructures with enhanced overall optical emission can enable us to rationally utilize these composites for photovoltaic applications.

In fact, the optoelectronic properties of the 0D-0D, 0D-1D, and 0D-3D CdSe QD-NaYF₄ nanocomposites, respectively, are measurably different, and are affected to a large extent by differential QD coverage densities on the underlying fluoride motifs. Therefore, we believe that our work has provided an experimental basis for optimizing analogous upconversion material - QD-based hybrid systems, which represent promising candidates as functional components for the next generation of QD-sensitized solar cell configurations.

**Supporting Information.** Electronic supplementary information (ESI), including structural and optical characterization data, is available.

**Acknowledgements**

Funds for research work (including support for all authors) at Brookhaven National Laboratory (BNL) were provided by the U.S. Department of Energy (DOE), Office of Basic
Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-SC-00112704. Moreover, this research used instrumentation resources (including electron microscopy and optical spectroscopy) of the Center for Functional Nanomaterials, also located at Brookhaven National Laboratory and funded under Contract No. DE-SC-00112704.
References


Figure 1. SEM images of as-prepared NaYF₄ samples, after reaction times of (A) 1 h, (B) 2 h, (C) 4 h, and (D) 6 h, respectively. The reaction temperature has been fixed at 100°C, whereas the ammonia concentration has remained constant at 0.2 M for all four samples shown herein.
Figure 2. SEM images of as-prepared NaYF₄ samples, created with reaction temperatures of (A) 100°C, (B) 140°C, (C) 180°C, and (D) 220°C, respectively. The reaction time has been fixed at 2 h, while the ammonia concentration has remained constant at 0.2 M, for all four samples shown herein.
Figure 3. Representative SEM images of as-prepared NaYF$_4$ samples, created with *ammonia concentrations* of (A) 0 M, (B) 0.2 M, (C) 0.4 M, and (D) 0.8 M, respectively. The reaction time has been fixed at 2 h, while the reaction temperature has been set at 100°C, for all four samples herein.
Figure 4. Representative (A) TEM image and (B) corresponding high-resolution TEM image of \( \alpha \)-phase nanoparticles. Typical (C) TEM images and (D) coupled high-resolution TEM image of \( \beta \)-phase nanowire bundles. The insets to (B) and (D) are associated SAED patterns of these respective regions of the sample.
Figure 5. **Top:** Schematic representation of the effect of reaction time/reaction temperature upon the growth mechanism of as-prepared NaYF₄ nanocrystals. **Bottom:** Schematic representation of the effect of the concentration of NH₃·H₂O upon the growth mechanism of as-prepared NaYF₄ nanocrystals.
Figure 6. (A) Upconversion PL emission spectra of NaYF₄: Ln³⁺ nanocrystals excited by a 980 nm laser. Four different curves represent samples synthesized with 0 M ammonia, i.e. nanoparticles (black); samples generated with 0.2 M ammonia, i.e. aggregated nanospheres (red); sample produced with 0.4 M ammonia, i.e. chromosomal-shaped motifs (blue); and samples fabricated with 0.8 M ammonia, i.e. nanowire bundles (pink), respectively. (B) The corresponding energy diagram is presented, highlighting all of the relevant transitions. Adapted and revised from an analogous diagram in reference 47.
Figure 7. Representative TEM images of heterostructures composed of (i) CdSe quantum dots attached to (ii) 0D and (iii) 3D NaYF₄ nanostructures, which had been synthesized with (A) 0 M ammonia, (B) 0.2 M ammonia, (C) 0.4 M ammonia, and (D) 0.8 M ammonia, respectively, as well as of (iv) separately-prepared (E) 1D NaYF₄ nanorods, respectively.
Figure 8. Representative STEM images as well as elemental mapping data associated with heterostructures composed of CdSe QDs coupled with 0D NaYF$_4$ (leftmost column), 1D NaYF$_4$ (middle column), and 3D NaYF$_4$ (right-side column), respectively. Scale bars for the three columns are 0.5 µm, 200 nm, and 2 µm, respectively.
Figure 9. Upconversion data associated with heterostructures composed of (i) CdSe QDs attached to (ii) 0D and (iii) 3D NaYF₄ samples, which had been synthesized with (A) 0 M ammonia, (B) 0.2 M ammonia, (C) 0.4 M ammonia, and (D) 0.8 M ammonia, respectively, as well as onto (iv) separately prepared 1D NaYF₄ nanorods (E), respectively.
Figure 10. Energy diagram, highlighting all of the expected relevant transitions within as-prepared CdSe-NaYF$_4$ heterostructures. Figure was prepared with relevant information obtained from references 31 and 47.
<table>
<thead>
<tr>
<th>Sample Preparation conditions, phase, and crystallinity</th>
<th>Morphology and Dimensions</th>
<th>Surface Area (m²/g)</th>
<th>QD loading within resulting heterostructures (CdSe: NaYF₄ molar ratio)</th>
<th>Estimated number of QDs per 10⁶ nm³ of the underlying NaYF₄ motif</th>
<th>FRET efficiencies (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M ammonia NaYF₄, α-phase, polycrystalline</td>
<td>0D Nanoparticles: average diameters of ~ 150 nm</td>
<td>13.9</td>
<td>0.32</td>
<td>3160</td>
<td>51%</td>
</tr>
<tr>
<td>0.2 M ammonia NaYF₄, α-phase, polycrystalline</td>
<td>Porous 0D Nanoparticles: average diameters of ~ 300 nm</td>
<td>21.7</td>
<td>0.68</td>
<td>6720</td>
<td>73%</td>
</tr>
<tr>
<td>0.4 M ammonia NaYF₄, β-phase, polycrystalline</td>
<td>3D Micron-sized chromosomal motifs: Overall average diameters of ~2 µm with lengths of ~ 5-8 µm</td>
<td>11.7</td>
<td>0.21</td>
<td>2340</td>
<td>48%</td>
</tr>
<tr>
<td>0.8 M ammonia NaYF₄, β-phase, polycrystalline</td>
<td>3D Micron-sized nanowire bundles: Overall average diameters of ~1.5 µm with lengths of ~ 5 µm</td>
<td>14.9</td>
<td>0.29</td>
<td>3240</td>
<td>57%</td>
</tr>
<tr>
<td>1D NaYF₄, β-phase, single crystalline</td>
<td>1D Nanorods: Average diameters of ~ 100-200 nm with lengths of ~ 1 µm</td>
<td>5.8</td>
<td>0.11</td>
<td>1230</td>
<td>27%</td>
</tr>
</tbody>
</table>

**Table 1.** Summary of the physical surface area data, calculated from BET results, the relevant quantum dot loading values and estimated numbers of quantum dots onto variously as-prepared heterostructures, as well as the energy transfer efficiencies of these heterostructures.
**TOC entry**: FRET efficiency between CdSe QDs and NaYF₄ is affected by the amount of QD loading onto the underlying 0D, 1D, and 3D NaYF₄ host materials.