pH Mediated Control Synthesis of Lanthanide-Doped YPO$_4$ Upconversion Nano/Microcrystals

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Abstract: A pH-mediated rational control over the phase transformation, morphology and size of lanthanide doped YPO$_4$ nano/microcrystals has been accomplished using a hydrothermal route. The morphology of the resulting particles evolves from the spheres, to the nanoflakes and finally to the nanorods when increasing the pH value of the reaction solution from 1 to 9, while the induction of crystal phase transformation from a tetragonal structure to a hexagonal structure takes place at pH = 5. When excited at 980 nm, the hexagonal phase YPO$_4$•0.8H$_2$O: 18%Yb$^{3+}$, 2%Er$^{3+}$ nanoflakes prepared at pH = 7 exhibit the strongest UC emission intensity among investigated samples of varying size, phase and morphologies. This work provides a paradigm on the controlled synthesis of lanthanide doped upconverting orthophosphates, which hold great promise for various photonic and biophotonic applications.

Keywords: Orthophosphate, Morphology, Upconversion

Introduction

Frequency Upconversion (UC) in nano/microcrystals doped with trivalent Lanthanide (Ln$^{3+}$) ions has attracted wide attentions in recent years due to its potential application in many fields such as volumetric multicolor displays (Downing et al., 1996), solar cells (Chen et al., 2013a), bioimaging (Chen et al., 2014; 2012), drug delivery (Hou et al., 2011; Tian et al., 2012) and photodynamic therapy (Shan et al., 2011; Zhang et al., 2007). They are able to convert two or more photons, typically Near Infrared (NIR) light, into shorter wavelength visible or ultraviolet emission (Chen et al., 2014). To realize highly efficient UC emissions, various host matrices have been extensively studied to provide an appropriate local crystal field effect for the incorporated lanthanide ions, alongside their conspicuous physiochemical properties (Chen et al., 2014). Among investigated Ln$^{3+}$ doped nano/microcrystals of varying host lattices, the Ln$^{3+}$ doped orthophosphates hold great promise in most of aforementioned technological applications, as the orthophosphate host lattice possesses excellent physicochemical and optical stabilities under high temperature and high energy excitations and enables the Ln$^{3+}$ ions to illuminate at a high efficiency (Balakrishnaiah et al., 2009; Di et al., 2007; 2005; Meyssamy et al., 1999; 2001).

Previously, Ln$^{3+}$ doped orthophosphate particles have been typically used as typical downconversion (or Stokes type) luminophores whereby the emission wavelength is longer than the excitation wavelength. They have been considered as one of the promising candidates for Plasma Display Panel (PDP) applications due to their high absorption, high thermal and chemical stabilities (Balakrishnaiah et al., 2009; Di et al., 2007; 2005). Hasse and co-workers have successfully synthesized LaPO$_4$ downconversion particles via wet-chemical method for such purpose, whereby the phase structure of resulting products was controlled by changing the temperature used for crystallization (Meyssamy et al., 1999). A later work reported by the same group indicates that a luminescence quantum yield up to 61% can be achieved in this luminescent Ce$^{3+}$/Tb$^{3+}$ codoped downconversion nanoparticles (Meyssamy et al., 2001). The reported low toxicity and luminescence stability allow these Ln$^{3+}$ doped LaPO$_4$ to be potentially used as biolabels towards clinical practices (Hutchison 1999; de Sousa Filho and Serra, 2011; Meiser et al., 2004).
The Ln³⁺ doped YPO₄ particles is an analogy of the Ln³⁺ doped LaPO₄ particles due to the similarities between the Y and the La rare earth element as well as the identical structures of both materials. Indeed, Li et al. (2009) reported that YPO₄ particles doped with Ln³⁺ (Ln = Tb, Eu, Dy) and Y³⁺ ions nano/microcrystals have superior downconversion emissions. These results make both LaPO₄ and YPO₄ host materials attractive toward various optically related applications. However, all these reported works are related to the downconversion (or Stokes-shifted) emission properties (Luwang et al., 2011; Mai et al., 2007; Yang et al., 2009; Li et al., 2009). Limited attentions have been paid to the upconversion (or anti-Stokes shifted) luminesce of Ln³⁺ doped orthophosphate particles.

A pertinent attempt has been made to dope the sensitizer Yb³⁺ and the activator Er³⁺ into the bulk single crystal LaPO₄ host material. An efficient visible upconversion has been realized upon excitation at 980 nm in the codoped single crystal due to the efficient energy transfer from Yb³⁺ to Er³⁺ ions and the strong absorption ability of Yb³⁺ ions (Lisiecki et al., 2009). In addition, intense NIR to visible frequency upconversion luminescence has also been reported in single Er³⁺-doped YPO₄ phosphors (Balakrishnaiah et al., 2010). Both results suggest that the LnPO₄ material is promising host lattice for Ln³⁺ ions to produce superior upconversion luminescence along the well-established fact on producing efficient downconversion luminescence. It is well known that the morphology, the phase structure and the size of the resulting particles are of particular importance for their performance to meet the needs for specific applications. These parameters also play a significant role in defining the upconverting luminescence properties, as manifested in Ln³⁺ doped fluoride particles (NaYF₄, NaLuF₄, LuF₃, etc) (Dou and Zhang, 2011; Hao et al., 2014; Li et al., 2008; Hao et al., 2012). However, until this moment, there lacks facile routes to synthesize and to rationally control the phase transformation, the morphology, as well as the size of Ln³⁺ doped YPO₄ upconverting nano/microparticles. Moreover, the impact of the morphology and phase on the UC luminescence from Ln³⁺ doped YPO₄ nano/microcrystals remained unexplored.

Herein, we report on the controlled synthesis of the tetragonal YPO₄:18%Yb³⁺,2%Er³⁺ and the hexagonal YPO₄:0.8H₂O: 18%Yb³⁺,2%Er³⁺ nano/microcrystals with uniform and tunable size via a hydrothermal route. It is worth noting that the common hydrophilic chelating agent of trisodium citrate (for the preparation of down conversion orthophosphate particles) is replaced by the lipophilic chelating agent of Oleic Acid (OA) in the current preparing procedure, which has seldom been investigated before for the synthesis of Ln³⁺ doped YPO₄ particles. We demonstrate that the pH value of the reaction solution plays a significant role in determination of the morphology and the phase of the resulting YPO₄:Yb³⁺/Er³⁺ particles. Furthermore, we show that the hexagonal phase YPO₄•0.8H₂O: 18%Yb³⁺,2%Er³⁺ nanoflakes exhibit the strongest UC emission intensity among the resulting particles of varying morphologies. Based on the observed 4f-4f transitions of trivalent lanthanide ions, we also discuss the possible upconverting pathways of the Yb³⁺/Er³⁺ codoped YPO₄ nano/micrometer particles.

**Experimental**

All the reagents were purchased from Tianjin Chemical Reagents Co.Ltd. and used as raw materials without further purification.

About 1.2 g NaOH was firstly dissolved in 3 mL distilled H₂O under vigorous stir; after that 5 mL ethanol and 18 mL OA were added in order into the above aqueous solution. The agitation lasted 30 min before 2 mL of Ln(NO₃)₃•6H₂O (0.5 M) (Y³⁺:Yb³⁺:Er³⁺ = 80:18:2) was added into the above faint yellow viscous solution. After that, 2 mL of NH₄H₂PO₄ (1.5 M) was added into the above milky mixture in 10 min. Then the mixing solution was transferred into a 50 mL Teflon bottle held in a stainless steel autoclave, sealed tightly and maintained steadily at 180°C for 24 h. After cooling down to room temperature naturally, the precipitates were collected by centrifugation and washed with deionized water and ethanol in sequence for several time and then dried in air at 60°C for 12 h. The samples with various morphologies were synthesized using the same protocol and parameters except by adjusting the pH value of the reaction solution before transferring to the hydrothermal reactor (i.e., pH = 1, 3, 5, 7 and 9) via the adding NaOH (5 M) or HNO₃ (5 M). The synthesis process of hexagonal YPO₄•0.8H₂O submicromorphs referred to the literature procedure (Li et al., 2009) with the difference in doping different types and amount of trivalent lanthanide ions.

The X-Ray powder Diffraction (XRD) pattern was carried out with a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Ka source (λ = 0.154056 nm). Micrographs for the prepared samples were obtained using a Field Emission Scanning Electron Microscope (FESEM, MX2600FE). The as-prepared powders were pressed to form a smooth and flat disk to be utilized for spectral studies by irradiation with 980 nm diode laser (Hi-Tech Optoelectronics Co. Ltd, Beijing). The emitted UC fluorescence was collected by a lens-coupled monochromator (Zolix Instruments Co. Ltd, Beijing) of 2 nm spectral resolution with an attached photomultiplier tube (Hamamatsu CR131).
Results and Discussion

The pH value of the initial reaction solution exerts a large impact on the phase and morphology of the resulting Yb$^{3+}$, Er$^{3+}$ doped YPO$_4$ nano/microcrystals. The crystal phases of the resulting products were measured and identified by the XRD technique. The XRD patterns of the samples synthesized with the stabilizing agent of OA under different pH conditions (i.e., pH = 1, 3, 5, 7 and 9) are all shown in Fig. 1. As one can see in Fig. 1, a tetragonal YPO$_4$ structure is adopted for the products when the pH value is below 3 under the current synthesizing condition. However, when the pH value is increased from 3 to 5, a new hexagonal phase of YPO$_4$•0.8H$_2$O appears, manifesting the occurrence of a phase transformation. With further increasing the pH value to and exceeding 7, the pure hexagonal phase YPO$_4$•0.8H$_2$O (ICPDS No. 42-0082) particles were obtained. Therefore, it can be concluded that the change of pH value of the initial reaction solution can induce the phase transformation from the tetragonal phase to the hexagonal phase, along with dramatic morphology changes of the products (consulted Fig. 2). Moreover, Fig. 1 displays a large difference in the relative intensities of the XRD diffraction peaks for samples of either the tetragonal phase or the hexagonal phase, revealing a preferential orientation growth along some crystal directions. In particular, the resulting products prepared at pH equal or below 3 exhibit much stronger diffraction peak intensities than the sample prepared at pH = 9.

The FESEM images provide direct information about the shape and size of the Yb$^{3+}$/Er$^{3+}$ codoped YPO$_4$ samples prepared at different pH values (Fig. 2). The tetragonal phase YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ forms prepared at pH = 1, are round shape particles of 1 µm, defined by the aggregation of numerous nanoparticles (Fig. 2a). The type and concentration of lanthanide dopants were confirmed by energy dispersive x-ray spectrum (data not shown). When the pH is increased to 3, the tetragonal phase YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ forms tend to grow into regular shape nanoparticles with an average size of 90 nm, as shown in Fig. 2b. However, when the pH is equal to 5, significant change takes place in the morphology. Two distinct morphologies appear, including the small round shape nanoparticles (~90 nm) and the rod shape nanoparticles (90 nm ×1 µm), as shown in Fig. 2c. This observation in good agreement with the XRD result of coexisting the tetragonal YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ phase and the hexagonal YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ phase at pH = 5 (Fig. 2). When the pH value of the reaction system is increased to 7, uniform nanoflakes were generated, as shown in Fig. 2d. The FESEM images of the sample synthesized at pH = 9 reveals the products are nanorods shape (Fig. 2e). Compiling the results from the XRD and FESEM measurements, we can conclude that the pH value of the initial reaction solution play a vital role in determination of the phase and the morphology transition of the resulting particles. The higher pH value facilitates the formation of larger size particles with regular shape and lower crystal symmetry. The pH-induced morphology change can be attributed to the fact that the absorption abilities of the OA on certain crystal facets are regulated by the electrostatic interaction between the carboxylic group and the trivalent Ln$^{3+}$ ions, which are very sensitive to the pH value of the reaction solution (Li et al., 2007). It is known that the UC luminescence intensity is dependent on the phase, the size and morphology of the particles (Chen et al., 2014). As a result, the pH-induced phase, size and morphology change will produce a pronounced effect on the UC luminescence intensity. Moreover, regular submicron sized hexagonal YPO$_4$•0.8H$_2$O prisms (Fig. 2) were also synthesized using the commonly used hydrophilic trisodium citrate as a chelating agent, in order to provide a reference for optical comparison with the particles prepared in this work using the lipophilic OA as the chelating agent.

To evaluate the effect of the phase and morphology on the UC luminescent properties of YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ and YPO$_4$•0.8H$_2$O: 18%Yb$^{3+}$,2%Er$^{3+}$ particles, the resulting samples were excited by a 980 nm laser with excitation power density of ~390 W/cm$^2$ at room temperature and all the signal were collected under exactly identical conditions (Fig. 3). The luminescence emission spectra of the resulting samples of varying morphology are discerned using color-encoded lines, the tetragonal phase nanoparticles prepared at pH = 3 (black line), the mixed tetragonal and hexagonal phase particles prepared at pH = 5 (red line), the hexagonal phase nanoflakes prepared at pH = 7 (blue line), the hexagonal phase nanorods prepared at pH = 9 (violet line) and the reference hexagonal phase submicroprisms using trisodium citrate as the chelating agent (green line). As one can be seen in Fig. 3, three main emission UC peaks centered at 521, 540 and 654 nm were observed, one can be seen in Fig. 3, three main emission UC peaks centered at 521, 540 and 654 nm were observed, while the position and the shape of all the emission spectra are similar, with the exclusive difference in the relative intensities between the distinct emission bands. The hexagonal phase YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ nanoflakes prepared at pH = 7 show the highest emission intensity, while the tetragonal phase nanoparticles prepared at pH = 3, the mixed phase nanoparticles prepared at pH = 5 and the hexagonal phase nanorod prepared at pH = 9 display the lowest intensities of similar magnitude.
Fig. 1. The XRD patterns of the as-prepared YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ samples at different pH values of (a) 1, (b) 3, (c) 5, (d) 7 and (e) 9. The standard XRD patterns of hexagonal phase YPO$_4$•0.8H$_2$O (JCPDS 42-0082) and tetragonal phase YPO$_4$ (JCPDS 11-0254) are included as references.

Fig. 2. FESEM images for YPO$_4$ and YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ samples prepared with different pH values using the OA as chelating agent: (a) pH = 1; (b) pH = 3; (c) pH = 5; (d) pH = 7; (e) pH = 9 and (f) trisodium citrate as chelating agent.
Fig. 3. UC Photoluminescence (PL) spectra of YPO$_4$ and YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ samples with different pH values under diode laser excitation at 980 nm. Excitation power density, ~390 W/cm$^2$

Furthermore, the intensity of the hexagonal phase YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ nanoflakes (average 3 µm in size and 30 nm thick) prepared using the OA as chelating agent is almost 2 times as high as that of YPO$_4$•0.8H$_2$O:18%Yb$^{3+}$,2%Er$^{3+}$ submicron microprisms (~700 nm in size and ~350 nm thick) prepared using trisodium citrate as chelating agent. The difference in UC luminescence intensities among all investigated samples can be attributed to the combined roles of the phase, morphology and the particle sizes. The samples of hexagonal phase with higher crystallinity and larger size tend to emit stronger UC emission intensity. This is because (i) the smaller surface-to-volume ratio the particle processes, the fewer surface lanthanide ions will be exposed to surface quenching sites, thus the lesser the surface-related quenching effect will be created; (ii) the lower crystal phase favors the higher UC emission intensity, due to the lessened constraint on the forbidden dipole-dipole nature of the f-f transition; (iii) the higher crystalline in the resulting particles produces less crystal defects to provide quenching effects, thus favoring the UC emission intensity (Downing et al., 1996; Chen et al., 2013b).

In order to understand the UC mechanism of the Yb$^{3+}$/Er$^{3+}$ co-doped YPO$_4$ system, the dependence of the upconverted visible emission intensities on the laser pump power were measured and displayed in a logarithmic scale in Fig. 4. For the unsaturated conditions, the formulation $I_{UC} \propto P^n$ can be used to quantify the number of photons that are involved for the population of the upper emitting state; where the $I_{UC}$ is the luminescence emission intensity from the upper emitting state, $P$ is the pump laser power and $n$ is the number of the laser photons involved. The fitting slope of the experimental data in a double logarithmic plot can accurately provide the photon numbers, as shown in Fig. 4. For the hexagonal phase Yb$^{3+}$/Er$^{3+}$ co-doped YPO$_4$ nanoflakes prepared at pH = 7, the $n$ values of 2.08, 2.03 and 1.89 were obtained for the UC emission peaks at 521 nm (green), 540 nm (green), 654 nm (red), respectively. These slope values demonstrates that a two-photon process is responsible for both the green and the red UC emissions, for Yb$^{3+}$/Er$^{3+}$ co-doped YPO$_4$ nano/microcrystals of varying morphologies and phases.

Figure 5 displays the energy levels of the Yb$^{3+}$ and Er$^{3+}$ as well as the proposed UC mechanisms involved to produce the upconverted emission bands in Fig. 3. Firstly, the Yb$^{3+}$ ion absorbs one laser photon and is excited from the ground $^2$F$_{7/2}$ state to the $^2$F$_{5/2}$ state. The release of the energy via the first Yb$^{3+} \rightarrow$ Er$^{3+}$ energy transfer excites the Er$^{3+}$ ions from the $^4$I$_{15/2}$ state to the $^4$I$_{11/2}$. Then, the Er$^{3+}$ ion is further promoted to the $^4$F$_{7/2}$ state through a second Yb$^{3+} \rightarrow$ Er$^{3+}$ energy transfer process. The $^4$H$_{11/2}$ and $^4$S$_{3/2}$ states can be populated by nonradiative relaxations from the $^4$F$_{7/2}$ state, which generate the 521 and 540 nm emissions by radiative decay to the ground state. In addition, the red emission centered at 654 nm can be
acquired through the radiative transition from the $^4F_{9/2}$ (Er$^{3+}$) to the $^4I_{15/2}$ (Er$^{3+}$) state. Here, the $^4F_{9/2}$ (Er$^{3+}$) state can be populated by a nonradiative decay from the $^4S_{3/2}$ state (Er$^{3+}$) involving the assistance of phonons from the YPO$_4$ host lattice. It is noted that the green upconversion emission show stronger intensity than that of the red emission. This might be attributed to the large energy gap (~3059 cm$^{-1}$) between the $^4S_{3/2}$ state and the $^4F_{9/2}$ state, resulting in inefficient nonradiative deactivations to populate the $^4F_{9/2}$ state and thus producing the weak red UC emissions.

Conclusion
In summary, we have developed a facile hydrothermal route to prepare Yb$^{3+}$/Er$^{3+}$ co-doped YPO$_4$ nano/microcrystals with pH-controlled morphologies and sizes using the OA as the chelating agent. Moreover, the YPO$_4$ nanoparticles, nanoflakes and nanorods can be easily obtained via simply tuning the pH value (from 1 to 9) of the reaction solution while keep all other reaction parameters the same. Moreover, a phase transformation from the tetragonal YPO$_4$:18%Yb$^{3+}$,2%Er$^{3+}$ nanoparticles to the hexagonal YPO$_4$:0.8H$_2$O: 18%Yb$^{3+}$,2%Er$^{3+}$ particles can also be induced by increasing the pH value from 3 to 5. Furthermore, spectroscopic investigations of the resulting particles revealed a phase-, morphology- and size-dependent UC luminescence when excited at ~980 nm. The highest UC luminescence intensity was from the hexagonal YPO$_4$:0.8H$_2$O: 18%Yb$^{3+}$,2%Er$^{3+}$ nanoflakes prepared at pH = 7. Additionally, the UC emission mechanism is also studied in details. This work provides a pilot investigation on developing lanthanide doped upconverting orthophosphates of varying size, phase and morphology for future photonic and biophotonic applications.

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Author’s Contributions
Meiling Tan: Performed the experiment, drafted the manuscript
Shuwei Hao: Performed the experiments, analyzed the data, edited the manuscript.
Xiangbin Meng: Performed the experiments, analyzed the data.
Jing Liu and Yunfei Shang: Data analysis.
Chunhui Yang: Developed the idea, supervised the experiments, analyzed the data, edited the manuscript
Guanying Chen: Developed the idea, supervised the experiments, analyzed the data and edited the manuscript.

Ethics
The authors would like to disclose that Dr. Guanying Chen is an editorial board member for the American Journal of Engineering and Applied Sciences.
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