Research Article

Intense Red Upconversion Emission and Shape Controlled Synthesis of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ Nanocrystals

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Yb/Er codoped $\text{Gd}(\text{OH})_3$ was synthesized firstly via a simple hydrothermal treatment of the corresponding nitrate in the presence of alkali by tuning the pH values. The $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals were obtained via sintering the corresponding hydroxides precursors. The as-prepared samples were characterized by the typical X-ray diffraction, energy-dispersive X-ray spectroscopy, transmission electron microscopy (TEM), high-resolution TEM, and spectrophotometer. The results revealed that two shapes of the as-prepared $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals can be readily tuned from lemon-like particle to rod-like structure via tuning pH values from 7 to 14. Moreover, compared with the samples prepared at pH 7, the $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals prepared at pH 14 exhibit enhanced red upconversion emission and higher upconversion luminescence intensity under the excitation of 980 nm laser.

1. Introduction

Rare-earth (RE) doped upconversion (UC) nanocrystals have been comprehensively used in high-quality lighting devices, magnets, and other functional materials due to their optical, electronic, and chemical properties arising from the 4f shell of their ions [1–6]. These capabilities are highly sensitive to the bonding states of RE ions. RE doping induced photoluminescence property in fluorides, and oxides systems have been universally reported [7–11]. For instance, Yb/Tm codoped Y_2O_3 nanocrystals can achieve remarkable green UC luminescent emission [8]. In Yb/Er codoped Lu_2O_3 system, UC spectra revealed that simultaneous green and red emissions can be obtained [11]. However, the intense UC emission located in the red region by doping Yb/Er is an enormous challenge owing to the fact that Yb/Er codoped UC materials have a multipeak emissions nature. Recently, Li's group have developed a simple and controlled synthetic method [3–5], in which the shape transformation, phase evolution, and UC emission tuning of a series of RE oxides nanocrystals can be reached by simply adjusting reaction parameters, such as pH value, reaction time, and temperature.

Among various developed RE-based oxides UC nanomaterials, gadolinium oxide (Gd_2O_3) has its unique UC luminescent and magnetic properties. Therefore, RE (Nd^{3+} , Er^{3+} , and Tm^{3+}) doped Gd_2O_3 nanocrystals have been selected for optical and magnetic studies, because of their high chemical durability, photothermal and photochemical stabilities, low photon-energy, and unpaired electrons of the 4f shell [12–17]. Of course, there are also many investigations of the UC luminescence nanocrystals mainly focused on the RE doped Gd_2O_3 with phase/structure control and UC luminescence tuning [15, 18–20]. Even though UC emissions of RE doped Gd_2O_3 nanocrystals can be enhanced via changing reaction parameters, intense red UC emission is still a large challenge for the various energy levels of RE ions. In general, these nanocrystals exhibit multipeak UC emissions due to the fact that the doped lanthanide ions have abundant energy levels. However, there are still limited reports about doping Yb/Er to achieve intense red UC emission.

In this work, the precursor $\text{Gd}(\text{OH})_3$ codoped with Yb^{3+} and Er^{3+} ions was synthesized at first via a simple hydrothermal reaction. After that, the nanoparticle and nanorod structures of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ were obtained by calcination of the

corresponding $\text{Gd}(\text{OH})_3$ precursors prepared at different pH values of 7 and 14, respectively. The UC properties of the $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ samples with different shapes were studied. Interestingly, greatly enhanced red UC emission can be realized by simply tuning the pH value from 7 to 14, which will expand their application from optics to the biological field.

2. Experimental

2.1. Materials and Regents. $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Gd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$, 99.99%) was purchased from Sigma-Aldrich. KOH was purchased from Sinopharm Chemical Reagent Co., China. All of the reagents were used as received with no further purification.

2.2. Synthesis of Yb/Er Codoped $\text{Gd}(\text{OH})_3$ and Gd_2O_3 Nanocrystals. $\text{Gd}(\text{OH})_3\text{:Yb/Er}$ nanocrystals were synthesized by using a simple hydrothermal treatment [5] of the corresponding nitrate in the presence of alkali. In a typical synthesis, 1 mmol of $\text{Gd}(\text{NO}_3)_3$ (0.5 M), $\text{Yb}(\text{NO}_3)_3$ (0.5 M), and $\text{Er}(\text{NO}_3)_3$ (0.5 M) with the designed molar ratio of 78 : 20 : 2 was added into 20 mL of deionized (DI) water. And then, aqueous KOH (10 wt%) solution was added dropwise into the mixture until the pH was adjusted to a designated value (7/14). After another stirring for 20 min, the formed colloidal mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and then sealed and maintained at 180°C for 12 h. After the reaction was completed, the reaction system was permitted to cool to room temperature naturally and the pure solid product $\text{Gd}(\text{OH})_3\text{:Yb/Er}$ was obtained by washing with deionized water several times and drying at 60°C for 24 h. In addition, the corresponding oxide nanocrystals ($\text{Gd}_2\text{O}_3\text{:Yb/Er}$) have been prepared by calcination of $\text{Gd}(\text{OH})_3\text{:Yb/Er}$ at 450°C for 6 h.

2.3. Characterizations. Typical X-ray diffraction (XRD) patterns were recorded by a D/max- γ A System X-ray diffractometer at 40 kV and 250 mA with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). The shape and structure of the as-prepared samples were characterized by transmission electron microscopy (TEM, JEOL-2100F) equipped with the energy-dispersive X-ray spectroscopy (EDS). The UC emissions were tested by a spectrophotometer (R500) equipped with a 980 nm laser diode.

3. Results and Discussion

Crystal phase of the as-prepared $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ samples was identified by powder XRD pattern. After continuous heating for 6 hours at 450°C, $\text{Gd}(\text{OH})_3\text{:Yb/Er}$ (pH = 7) nanocrystals have completely transformed to $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ and the corresponding XRD analysis is showed in Figure 1(a). In addition, the phase of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7) has transformed into pure cubic phase and no other peaks have been detected. When the pH value is tuned up to 14, pure cubic phase of as-synthesized products can be obtained as well as presented in Figure 1(b). The diffraction peaks of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals (pH = 7/14)

FIGURE 1: XRD pattern of (a) $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7) and (b) $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 14) nanocrystals and (c) standard cubic phase Gd_2O_3 .

are well coincident with the peaks of the standard cubic phase Gd_2O_3 (JCPDS number 12-0797, Figure 1(c)).

To further investigate the morphology and structure of these nanocrystals, TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) assays were carried out. As shown in Figure 2(a), the precursor ($\text{Gd}(\text{OH})_3\text{:Yb/Er}$, pH = 7) presented lemon-like shape. Figure 2(c) shows a typical TEM image of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7). As demonstrated, the samples presented lemon- and rod-like structures. The interplanar spacing in the HRTEM image (Figure 2(d)) of a single particle was measured to be 3.10 Å, corresponding to the 111 crystal plane of cubic phase Gd_2O_3 , which is matched well with the XRD analysis. Figure 2(e) shows the typical SAED result, further validating the formation of body-centered cubic phase structure. To further study the influence on morphology by tuning pH value, the TEM image of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 14) is presented in Figure 2(f). As shown in Figure 2(f), compared with $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7), the shape was completely changed to pure rod-like morphology. Figure 2(h) shows the typical HRTEM image taken from an individual nanorod (Figure 2(g)). The interplanar spacing was measured to be 2.68 Å, which agrees well with the 400 crystal plane of cubic phase Gd_2O_3 , indicating the formation of cubic phase rod-like structure. The SAED result of nanorods (Figure 2(i)) also presents the characterized polycrystalline diffraction rings of body-centered cubic phase, further demonstrating the formation of cubic phase rod-like structure. Therefore, tuning pH value from 7 to 14 can successfully achieve the morphology evolution of Yb/Er codoped Gd_2O_3 nanocrystals from lemon-like particle to rod. Figure 2(b) exhibits EDS analysis of the as-prepared $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 14), indicating that Gd, O, Yb, and Er are the major elements in these nanorods.

The UC luminescence property of the $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals was studied at room temperature. As shown in Figure 3, $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7) exhibits intense red and weak green emissions (green curve) under excitation by

FIGURE 2: (a) TEM image of $\text{Gd}(\text{OH})_3\text{:Yb/Er}$ (pH = 7). (b) EDS analysis of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanorods shown in (f). (c) TEM image of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 7) and the corresponding (d) HRTEM and (e) SAED, respectively. (f) TEM image of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ (pH = 14). (g) TEM image of a single nanorod and (h) the corresponding HRTEM image. (i) The SAED characterization of nanorods shown in (f).

FIGURE 3: UC spectra of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanocrystals with different pH values. The blue curve stands for pH = 7, and the red one corresponds with pH = 14.

FIGURE 4: Schematic energy-level diagram of Yb^{3+} and Er^{3+} ions.

continuous-wave 980 nm laser diode. Moreover, the later CIE calculated chromaticity coordinates (Figure 6) reveal that yellow light can be obtained. However, via varying the pH value from 7 to 14, the red UC emission efficiency and emission intensity of $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ have been extremely enhanced (red curve). As presented in Figure 4, the two green light

emissions (labeled by green arrows) are attributed to the electronic transitions $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{11/2}$, which correspond with the green emissions (Figure 3) centered in 525 and 538 nm, respectively. On the other hand, the red emission (labeled by the red arrow) is ascribed to the transition of $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$, which is well coincident with the red emission centered at 662 nm. To further reveal the UC emission property of these $\text{Gd}_2\text{O}_3\text{:Yb/Er}$ nanorods,

FIGURE 5: Dependence of PL spectra on pumping power in Gd_2O_3 :Yb/Er nanorods.

FIGURE 6: The CIE 1931 chromaticity diagram and calculated chromaticity coordinates. The red arrow indicates the changing tendency of chromaticity coordinate of Gd_2O_3 :Yb/Er nanorods (pH = 14) by increasing the excitation power.

power dependent UC spectra have been studied (Figure 5). With increasing excitation power, the as-synthesized samples exhibit the trend of enhancing UC luminescence, especially red emission, which can be observed obviously from the red arrow shown in the CIE diagram (Figure 6). It is noted that the dominant red UC emission with very weaker green UC emission in the Yb/Er doped system is mainly attributed to the fact that the intensity ratio of the red to green emissions increased rapidly and the green emissions almost quenched for high doped content of Yb^{3+} (20 mol%) [11, 21].

4. Conclusions

In conclusion, body-centered cubic phase Gd_2O_3 :Yb/Er nanocrystals with different shapes were successfully synthesized by a hydrothermal method and combination of

a subsequent calcination. By tuning the pH value of the reaction system, the shape of Gd_2O_3 :Yb/Er nanocrystals can be successfully tuned from lemon-like shape to rod. More interestingly, when adjusting the pH value from 7 to 14, the red UC emission and whole UC emission intensity have been remarkably enhanced. The bright red UC emission of these nanorods may expand their application varying from optics to the biological field.

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References

- [1] G.-Y. Adachi and N. Imanaka, "The binary rare earth oxides," *Chemical Reviews*, vol. 98, no. 4, pp. 1479–1514, 1998.
- [2] J. A. Capobianco, J. C. Boyer, F. Vetrone, A. Speghini, and M. Bettinelli, "Optical spectroscopy and upconversion studies of Ho^{3+} -doped bulk and nanocrystalline Y_2O_3 ," *Chemistry of Materials*, vol. 14, no. 7, pp. 2915–2921, 2002.
- [3] X. Wang, X.-M. Sun, D. P. Yu, B.-S. Zou, and Y. D. Li, "Rare earth compound nanotubes," *Advanced Materials*, vol. 15, no. 17, pp. 1442–1445, 2003.
- [4] Z.-L. Wang, J. H. Hao, H. L. W. Chan, W.-T. Wong, and K.-L. Wong, "A strategy for simultaneously realizing the cubic-to-hexagonal phase transition and controlling the small size of NaYF_4 : Yb^{3+} , Er^{3+} nanocrystals for in vitro cell imaging," *Small*, vol. 8, no. 12, pp. 1863–1868, 2012.
- [5] X. Wang and Y. D. Li, "Synthesis and characterization of lanthanide hydroxide single-crystal nanowires," *Angewandte Chemie International Edition*, vol. 41, no. 24, pp. 4790–4793, 2002.
- [6] J. J. Zhou, G. X. Chen, E. Wu et al., "Ultrasensitive polarized up-conversion of Tm^{3+} - Yb^{3+} doped β - NaYF_4 single nanorod," *Nano Letters*, vol. 13, no. 5, pp. 2241–2246, 2013.
- [7] G. Z. Ren, S. J. Zeng, and J. H. Hao, "Tunable multicolor upconversion emissions and paramagnetic property of monodispersed bifunctional lanthanide-doped NaGdF_4 nanorods," *Journal of Physical Chemistry C*, vol. 115, no. 41, pp. 20141–20147, 2011.
- [8] S. F. Zhou, N. J. Jiang, K. Miura et al., "Simultaneous tailoring of phase evolution and dopant distribution in the glassy phase for controllable luminescence," *Journal of the American Chemical Society*, vol. 132, no. 50, pp. 17945–17952, 2010.
- [9] S. J. Zeng, J. J. Xiao, Q. B. Yang, and J. H. Hao, "Bi-functional NaLuF_4 : Gd^{3+} / Yb^{3+} / Tm^{3+} nanocrystals: structure controlled synthesis, near-infrared upconversion emission and tunable magnetic properties," *Journal of Materials Chemistry*, vol. 22, no. 19, pp. 9870–9874, 2012.
- [10] S. J. Zeng, M.-K. Tsang, C.-F. Chan, K.-L. Wong, and J. H. Hao, "PEG modified BaGdF_5 :Yb/Er nanoprobe for multi-modal upconversion fluorescent, *in vivo* X-ray computed tomography and biomagnetic imaging," *Biomaterials*, vol. 33, no. 36, pp. 9232–9238, 2012.

- [11] E. W. Barrera, M. C. Pujol, F. Díaz et al., "Emission properties of hydrothermal Yb^{3+} , Er^{3+} and Yb^{3+} , Tm^{3+} -codoped Lu_2O_3 nanorods: upconversion, cathodoluminescence and assessment of waveguide behavior," *Nanotechnology*, vol. 22, no. 7, Article ID 075205, 2011.
- [12] H. Guo, N. Dong, M. Yin, W. P. Zhang, L. R. Lou, and S. D. Xia, "Visible upconversion in rare earth ion-doped Gd_2O_3 nanocrystals," *Journal of Physical Chemistry B*, vol. 108, no. 50, pp. 19205–19209, 2004.
- [13] H. Guo, Y. F. Li, D. Y. Wang et al., "Blue upconversion of cubic $\text{Gd}_2\text{O}_3\text{:Er}$ produced by green laser," *Journal of Alloys and Compounds*, vol. 376, no. 1-2, pp. 23–27, 2004.
- [14] T. Hirai and T. Orikoshi, "Preparation of $\text{Gd}_2\text{O}_3\text{:Yb}$, Er and $\text{Gd}_2\text{O}_3\text{:Yb}$, Er infrared-to-visible conversion phosphor ultra-fine particles using an emulsion liquid membrane system," *Journal of Colloid and Interface Science*, vol. 269, no. 1, pp. 103–108, 2004.
- [15] D. Dosev, I. M. Kennedy, M. Godlewski, I. Gryczynski, K. Tomsia, and E. M. Goldys, "Fluorescence upconversion in Sm -doped Gd_2O_3 ," *Applied Physics Letters*, vol. 88, no. 1, Article ID 011906, 2006.
- [16] L. D. Sun, J. Yao, C. H. Liu, C. S. Liao, and C. H. Yan, "Rare earth activated nanosized oxide phosphors: synthesis and optical properties," *Journal of Luminescence*, vol. 87–89, pp. 447–450, 2000.
- [17] A. Brenier and G. Boulon, "Laser heated pedestal growth and spectroscopic investigations of Nd^{3+} -doped Gd_2O_3 single crystal fibres," *Journal of Luminescence*, vol. 82, no. 4, pp. 285–289, 1999.
- [18] A. Brenier, "Laser-heated pedestal growth of Er^{3+} -doped Gd_2O_3 single crystal fibres and up-conversion processes," *Chemical Physics Letters*, vol. 290, no. 4–6, pp. 329–334, 1998.
- [19] X. Bai, H. W. Song, G. H. Pan et al., "Improved upconversion luminescence properties of $\text{Gd}_2\text{O}_3\text{:Er}^{3+}/\text{Gd}_2\text{O}_3\text{:Yb}^{3+}$ core-shell nanorods," *Journal of Nanoscience and Nanotechnology*, vol. 9, no. 4, pp. 2677–2681, 2009.
- [20] M.-A. Fortin, R. M. P. Petoral Jr., F. Soderlind et al., "Polyethylene glycol-covered ultra-small Gd_2O_3 nanoparticles for positive contrast at 1.5 T magnetic resonance clinical scanning," *Nanotechnology*, vol. 18, no. 39, Article ID 395501, 2007.
- [21] Y. P. Li, J. H. Zhang, Y. S. Luo, X. Zhang, Z. D. Hao, and X. J. Wang, "Color control and white light generation of upconversion luminescence by operating dopant concentrations and pump densities in Yb^{3+} , Er^{3+} and Tm^{3+} tri-doped Lu_2O_3 nanocrystals," *Journal of Materials Chemistry*, vol. 21, no. 9, pp. 2895–2900, 2011.