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Upconversion Luminescence of Gd₂O₃:Ln³⁺ Nanorods for White Emission and Cellular Imaging via Surface Charging and Crystallinity Control

Mingda Wu,^{†‡} Guijian Guan,[‡] Bingqing Yao,[†] Choon-Peng Teng,[‡] Shuhua Liu,[‡] Si Yin Tee,[‡] Boon Chong Ong,[†] ZhiLi Dong,^{*,†} and Ming-Yong Han^{*,‡}

[†]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

[‡]Institute of Materials Research and Engineering, 2 Fusionopolis Way, Singapore 138634

*Corresponding to zldong@ntu.edu.sg and my-han@imre.a-star.edu.sg

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ABSTRACT. In this paper, an oxide matrix, Gd₂O₃, as an alternative counterpart of NaGdF₄ was developed via controlled surfactant-free synthesis, flexible lanthanide-loading, compositional/size tuning, hexagonal to cubic lattice-refinement and positive surface charging to achieve a substantial enhancement upconversion luminescence (~30 times upon calcination at 1000 vs. 600 °C; ~4000 times versus its hydroxide form) due to high crystallinity and extremely low residual impurities for white emission and cellular imaging.

INTRODUCTION

With fascinating features like large anti-Stokes shifts, sharp emission spectra and long excited-state lifetimes,¹⁻³ upconversion nanomaterials have attracted considerable attentions ranging from biological imaging,⁴⁻¹³ multiplexing responding,¹⁴⁻¹⁸ therapeutics,¹⁹⁻²⁶ security encoding,²⁷⁻³⁰ white-light generation³¹⁻³³ to volumetric display.³⁴⁻³⁵ Up to date, as a widely used matrix, NaYF₄ can effectively co-dope two different lanthanide ions (e.g. Yb³⁺/Er³⁺, Yb³⁺/Tm³⁺ or Yb³⁺/Ho³⁺) with optimized compositions to produce upconversion nanoparticles. In recent years, the partial or complete substitution of Y³⁺ by Gd³⁺ in NaYF₄ was demonstrated, and Gd³⁺ in the resulting NaGdF₄ matrix can mediate energy migration from Tm³⁺ to other emitting centers (e.g. Tb³⁺, Eu³⁺, Sm³⁺ and Dy³⁺) for achieving enriched upconversion luminescence.³⁶⁻³⁸ In addition to the cation substitution of Y³⁺ by Gd³⁺ in NaYF₄, the cation replacement of Gd³⁺ by other lanthanide ions (e.g. Tb³⁺, Eu³⁺, Dy³⁺ and Ce³⁺) in NaGdF₄ was also observed at mild conditions.³⁹⁻⁴⁰ In the same way, Na⁺ in NaGdF₄ was substituted by Ca²⁺ due to the stronger bonding dissociation energy of Ca-F than that of Na-F.⁴¹ The cation-exchange process was also observed during the production of NaGdF₄:Yb³⁺,Er³⁺@NaYF₄ core-shell structure, in which a solid solution formed at their interface because of intermixing between Y³⁺ and Gd³⁺.⁴²

Comparing to NaGdF₄, its oxide counterpart (Gd₂O₃), commonly prepared by calcination and used as MRI contrast agent⁴³ could be an alternative matrix to form more stable lanthanide-doped structure due to the higher bond dissociation energy (716 kJ/mol for Gd-O vs. 590 for Gd-F)⁴⁴ as indicated by the greatly increased melting temperature from 1231 (GdF₃) to 2420 °C (Gd₂O₃). Also, the rare earth fluorides have a certain solubility in water (e.g. 5.11×10⁻³ g for YF₃, 7.71×10⁻³ g for GdF₃, and 6.9×10⁻³ g for YbF₃ in 100 mL water),⁴⁵⁻⁴⁶ while the rare earth oxides

are more stable in aqueous circumstance, and the cations and anions inside are very difficult to be released from their crystals so as to render their high chemical stability and low bio-toxicity. Sol-gel and co-precipitation were used to produce irregular, porous or spherical $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanostructures in the presence of organic solvents or urea, and their weaker upconversion emission could be relevant to the residual impurities and polycrystalline nature from synthetic process and subsequent calcination.⁴⁷⁻⁵² Currently, there are a number of reports on the hydrothermal synthesis of crystalline $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ microstructures of sub- to micrometers in length/diameter.⁵³⁻⁵⁴ To achieve bright upconversion luminescence in this research, crystalline $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanostructures with greatly reduced dimension to ~ 100 nm in length and ~ 12 nm in diameter were readily produced by calcining crystalline $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ after prepared at much higher base/lanthanide ratios. Also, the fast growth at much smaller nanoscale enables their crystalline nature before and after calcination, and this can avoid the later stage growth at lower concentration to form defective microcrystals with more interfaces or boundaries during a long-time reaction. As such, a substantial enhancement upconversion luminescence has been achieved due to their high crystallinity and extremely low residual impurities when preparing in the absence of ligands and surfactants. Additionally, the greatly reduced possibility in cation migration in $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanostructures may contribute their use for applications in liquid/solid solutions.

Herein, we demonstrated a systematic loading of lanthanide dopant, Yb^{3+} into $\text{Gd}(\text{OH})_3$ with molar ratios ranging from 10, 20, 30, 40 to 50%. At 10-30%, pure $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}$ were formed while the $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}$ were observed together with $\text{Yb}_2\text{Cl}(\text{OH})_5 \cdot 1.5\text{H}_2\text{O}$ at 40-50% in a mixture. The doping flexibility was further revealed by doping with Er^{3+} to obtain $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ after thermal transformation at 1000°C , which exhibited a

upconversion enhancement for 4000 times compared to $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ prior to the calcination. It was found that the $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanorods in hexagonal phase was completely transformed into $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanorods in cubic phase at 600 °C. The increased crystallinity of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ at higher temperature (1000 vs. 600 °C) leads to a substantial enhancement in upconversion luminescence for 30 times, and the measured quantum yield of 1.6% was comparable to those of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ and $\text{NaGdF}_4:\text{Yb}^{3+},\text{Er}^{3+}$. It is noted that there are greatly reduced impurities or defects in nanorods when synthesizing in the absence of surfactants, which may also contribute to the substantial enhancement in upconversion. Interestingly, the calcined $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanorods were easily re-dispersed into water to exhibit individuals in their TEM images for various applications as probes in cellular uptake and imaging, and this indicates that there was no aggregation occurred during calcination, relevant to the surface repulsion between highly positively charged surfaces of neighboring nanorods. Moreover, the flexible co-doping of $\text{Yb}^{3+}/\text{Er}^{3+}$ or $\text{Yb}^{3+}/\text{Tm}^{3+}$ in Gd_2O_3 with various doping ratios (0-20% for Yb^{3+} , 0.1-10% for Er^{3+} , 0.1-2% for Tm^{3+} , respectively) was further demonstrated and optimized to achieve tunable emissions of RGB including white emission with desired proportions of individuals.

EXPERIMENTAL SECTION

Materials and synthesis. Gadolinium(III) chloride hexahydrate ($\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), erbium(III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), ytterbium(III) chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), and thulium(III) chloride hexahydrate ($\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) were purchased from Sigma-Aldrich. Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%) and sodium hydroxide (NaOH ,

99%) were obtained from Honeywell and Merck, respectively. Double distilled water was used through all the experiments.

To synthesize $\text{Gd}(\text{OH})_3$ rods, 0.6 mmol $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was first dissolved in 55 mL of water, and then added dropwise with 12 mmol ammonia (0.82 mL, 28 wt%) together with more water to form 60 mL of solution under vigorous stirring for half an hour. The solution comprised of 10 mM Gd^{3+} and 200 mM ammonia was then incubated at 160 °C for 6 h after transferred into a Teflon-lined stainless-steel autoclave. After cooling to room temperature naturally, the obtained $\text{Gd}(\text{OH})_3$ product was purified with water for three times and dispersed in water for further use. To investigate pH effect, the pH value of the solution was adjusted with a solution of 5 M NaOH in water before the hydrothermal synthesis of $\text{Gd}(\text{OH})_3$ rods.

To synthesize $\text{Gd}(\text{OH})_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Yb}, \text{Er}$ or Tm) rods with different doping levels, taking $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}$ as an example, $(0.6-x)$ mmol $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ and x mmol $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 55 mL of water prior to the addition of 12 mmol ammonia (0.82 mL, 28 wt%), 3.75 mmol NaOH (0.75 mL, 5M) and more water to form 60 mL of solution under vigorous stirring for half an hour. The resulting mixture at pH 12.5 was then incubated at 160 °C for 6 h after transferred into a Teflon-lined stainless-steel autoclave. After cooling to room temperature naturally, the obtained $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}$ precipitate was purified with double distilled water for three times and dispersed in water for further use. The purified product was also dried at 60 °C overnight before a calcination treatment at 400, 500, 600, 800 or 1000 °C with a ramp rate of 10°C/min. The resulting $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$ rods were readily dispersed in water for further characterization. To synthesize $\text{Gd}(\text{OH})_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Yb}, \text{Er}$ or Tm) rods with different co-doping levels, taking $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}, \text{Er}^{3+}$ as an example, $(0.6-x-y)$ mmol $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, x mmol

YbCl₃·6H₂O and y mmol ErCl₃·6H₂O were dissolved in 55 mL of water prior to the addition of 12 mmol ammonia (0.82 mL, 28 wt%), 3.75 mmol NaOH (0.75 mL, 5M) and more water to form 60 mL of solution under vigorous stirring for half an hour. The further procedure remains the same as the above.

Characterization. Upconversion emission spectra of the as-prepared colloids were recorded by Shimadzu RF-5301 PC fluorometer linked with a 980 nm laser. The decay curves of the upconversion emission were measured by using a customized phosphorescence lifetime spectrometer (FSP920-C, Edinburgh) equipped with a nanosecond optical parametric oscillator (OPO) NIR laser (980 nm) as the excitation source. The quantum yields were measured on the phosphorescence spectrometer equipped with a continuous-wave excitation source (980 nm).⁴⁰ The samples used for lifetime and quantum yields measurement were in the form of powder.

Transmission electron microscopy (TEM) images were collected on a Carl Zeiss Libra 120Plus transmission electron microscope operating at accelerating voltages of 120 kV. Scanning electron microscopy (SEM) images were obtained on a JEOL-7600F scanning electron microscope at accelerating voltage of 20 kV. X-ray diffraction (XRD) patterns was performed with a Shimadzu XRD-6000 system using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The samples were prepared by depositing and drying colloidal nanoparticles on copper grids, silicon substrates and glass slides for TEM, SEM and XRD characterization, respectively. Zeta-potential measurement was carried out by using Malvern Zetasizer.

Cytotoxicity study and upconversion fluorescence imaging *in vitro*. The CCD-112CoN cells were first seeded into a 96-well plate, and then cultured in DMEM supplemented with 10% FBS at 37 °C and 5% CO₂ for 24 h. After adding Gd₂O₃:6%Yb³⁺,1%Er³⁺ rods in water and

further incubating for 24 h at 37 °C, the cytotoxicity of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods at various concentrations (2 to 200 $\mu\text{g/mL}$) was determined using alamarBlue for three times. Similarly, the CCD-112CoN cells were grown on 14-mm glass coverslips in a 6-well plate. After washed with PBS, the cells were incubated in DMEM containing $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods (100 $\mu\text{g/mL}$) for 4 h followed by removing excessive rods with PBS prior to luminescence imaging in the range of 510-560 nm on a laser scanning confocal microscope (Leica TCS SP5 X, German) with the excitation wavelength of 980 nm.

RESULTS AND DISCUSSION

For this surfactant-free and hydrothermal synthesis of $\text{Gd}(\text{OH})_3$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was first dissolved in water and then added with 28 wt% ammonia dropwise to form a solution of 10 mM GdCl_3 together with 10, 40 or 200 mM ammonia under stirring for half an hour. Upon incubating at 160 °C for 6 h, $\text{Gd}(\text{OH})_3$ in hexagonal phase (space group: P63/m) were obtained with different morphologies under variable concentration of ammonia (**Figure 1a, Figure S1**). With 10 mM ammonia, irregular plates were found together with rods of ~55 nm in diameter and ~200 nm in length. With an increased concentration to 40 mM, only rods were obtained with diameter of ~90 nm and length of ~550 nm. At a much higher concentration of 200 mM, much larger rods with diameter of ~350 nm and length of ~1400 nm were observed (**Figure 1b**). By simply increasing the concentration of ammonia, the dimension of $\text{Gd}(\text{OH})_3$ rods increased but similar aspect ratio of 4-6 was retained, indicating the simultaneous growth in perpendicular and parallel directions in the absence of surfactant. In addition to the concentration-dependent preparation of $\text{Gd}(\text{OH})_3$ rods, the temperature effect was further investigated with the use of 10 mM GdCl_3 and 200 mM ammonia. With the increased temperature from 80, 120 to 160 °C, $\text{Gd}(\text{OH})_3$ rods were

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2
3 produced with reduced aspect ratio (**Figure 1c**). With the increased concentration of ammonia
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5 from 0 to 4 mM, the pH value increased quickly to 7.0, and then remained constant when
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7 increasing to 15 mM. This is followed by a steady increase to pH 9.2 and a very slow increase up
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9 to pH 9.7 in the concentration range of 15 $\rightarrow$ 80 mM and 80 $\rightarrow$ 200 mM (**Figure 1d**),
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11 respectively. It is clearly to see that there are three stages in this titration curve, and three
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13 concentrations of ammonia were chosen falling in the three stages.
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18 To increase in pH beyond 9.7, a small amount of strong base, NaOH instead of weak base,
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20 ammonia was used to quickly adjust the pH of reaction solutions to 10.0, 10.5, 11.0, 12.0 and
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22 12.5 followed by hydrothermal synthesis of Gd(OH)₃ rods at 160 °C for 6 h (**Figure 2a**). With
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24 the further increase in pH, there is a great reduction in both diameter and length of Gd(OH)₃ rods
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26 accompanied with increased aspect ratio first and then levelled off at pH 11 and above (**Figure**
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28 **2b**). At pH 12.5, more uniform nanorods of ~12 nm in diameter and ~95 nm in length were
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30 obtained, indicative of their fast nucleation to produce more uniform seeds in the presence of
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32 higher concentration of OH⁻ (similar case observed at pH 12). To understand the formation of
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34 monodispersed Gd(OH)₃ nanorods, the zeta-potentials of products formed at different pH (prior
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36 to hydrothermal synthesis) decreased quickly from +36.9, +33.9, +29.5, +22.3, +9.3 to -2.7 mV.
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38 Interestingly, the zeta-potentials of products after washing to pH 7, decreased first and then
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40 increased at pH 12 and above. The positive zeta-potentials indicate the presence of Gd³⁺ with
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42 non-stoichiometric reaction with OH⁻ (i.e. OH⁻/Gd³⁺ <3) on the surface of as-mixed products,
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44 accompanied with the coordination with neutral ammonia with Gd³⁺. With the increase in pH
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46 (i.e. OH⁻ concentration) up to 12.5, stoichiometric reaction of Gd³⁺ with OH⁻ tends to occur,
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48 leading to the decrease in positive charging to near neutral zeta-potential (**Figure 2c**). At pH
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50 12.5, the negative zeta-potential was -2.7 mV, and became more negative with further increase of
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pH to 13 (-27 mV), indicative of dominant adsorption of OH⁻ anions on the surface of rods at high concentration. After washing, the zeta-potential was measured to show greatly increase from -2.7 mV to +16.2 mV (**Figure 2c**). In this research, in the absence of organic ligands, a simple precipitate reaction was adopted to hydrothermally prepare Gd(OH)₃ nanorods under different pH values. At higher pH, the increased concentration/amount of OH⁻ may greatly accelerate the reaction with Gd³⁺ to form more nuclei, resulting in more smaller nanocrystals. The positive surface charging was apparently reduced even to negative for the product after mixing Gd³⁺ and ammonia at high pH 12.5 (**Figure 2c**). After washing, the zeta-potential was greatly increased to become positive again so as to remain their colloidal stability, indicating the stronger interaction of ammonia onto rare earth metal after removing excessive OH⁻.

The loading capacity of Gd(OH)₃ matrix was first assessed at pH 12.5 by incorporating Yb³⁺ to form Gd(OH)₃:xYb³⁺ nanorods at different doping levels of 10, 20, 30, 40, and 50 mol% (**Figure 3a**), in which x is equal to Yb³⁺/(Yb³⁺+Gd³⁺). When the loading ratio at Yb³⁺ ≤ 30 mol%, a pure hexagonal phase of Gd(OH)₃:Yb³⁺ was generated with homogeneous distribution of Yb³⁺ in nanorods (**Figure 3b**), identical to the hexagonal phase for the as-prepared Gd(OH)₃ without doping. At the increased loading ratio of Yb³⁺ up to 40 mol%, in addition to the characteristic peaks of hexagonal phase, a weak but clear XRD peak appeared at 11°, similar to the one for the orthorhombic phase of Yb₂Cl(OH)₅·1.5H₂O when synthesized by completely replacing Gd³⁺ with Yb³⁺ (the bottom plot in **Figure 3a**). After preparing with Yb³⁺ at 30 mol% and calcining the purified Gd(OH)₃:Yb³⁺ nanorods, there was a broad XRD band accompanied with a few sharp peaks after the thermal treatment of Gd(OH)₃:Yb³⁺ at 400 °C for 2h (**Figure 3c**). When calcined at 500 °C for 2h, only the characteristic XRD peaks of gadolinium oxide in cubic phase (space group Ia-3) were observed (**Figure S2**), indicating the complete transformation of

hexagonal $\text{Gd}(\text{OH})_3\text{:Yb}^{3+}$ to cubic $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}$. At the increased temperature of 600 °C, much shaper and stronger XRD peaks of resulting uniform $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}$ with ~120 nm in length and ~14 nm in diameter were observed to exhibit their enhanced crystallinity (**Figure 3c,d**).

To demonstrate upconversion luminescence, the co-doping of 1 mol% Er^{3+} and 10 mol% Yb^{3+} was further performed to form $\text{Gd}(\text{OH})_3\text{:10%Yb}^{3+}\text{:1%Er}^{3+}$ nanorods (**Figure 4a**). Under the excitation at 980 nm, there was no visible emission to our naked eyes. Upon calcination at 600 °C, characteristic upconversion luminescence was observed clearly. When further treating at 1000 °C, the luminescence became much stronger. The selected area electron diffractions (SAED) of the $\text{Gd}(\text{OH})_3\text{:Yb}^{3+}\text{:Er}^{3+}$ and $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}\text{:Er}^{3+}$ rods were examined with their low-resolution TEM images in insets (**Figure 4b and Figure S3**). After treated at 600 °C, only small arcs (i.e. slightly elongated diffraction spots) were observed in the SAED rather than clear spots for $\text{Gd}(\text{OH})_3\text{:Yb}^{3+}\text{:Er}^{3+}$ prior to calcination. However, the small arcs became clear spots after treatment at 1000 °C, indicating the greatly increased crystallinity at higher temperature. XRD results also support the increased crystallinity of $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}\text{:Er}^{3+}$ rods when increasing the annealing temperatures from 600, 800 to 1000 °C, indicated by their greatly decreased full-width at half maximum (FWHM) of XRD peaks (**Figure S4**). As shown in **Figure 4c**, high-resolution transmission electron microscopy (HRTEM) image of $\text{Gd}(\text{OH})_3\text{:Yb}^{3+}\text{:Er}^{3+}$ rods exhibited a preferential [0001] growth along the direction of rods, which corresponds to the [110] direction of $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}\text{:Er}^{3+}$ rods through thermal conversion at 1000 °C. Overall, the upconversion enhancement was obtained in two steps: (i) the thermal transformation from $\text{Gd}(\text{OH})_3\text{:Yb}^{3+}\text{:Er}^{3+}$ to $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}\text{:Er}^{3+}$ at 600 °C, and (ii) the thermal annealing to increase crystallinity of $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}\text{:Er}^{3+}$ at 1000 °C. In the first step, the enhancement arose from the decomposition of

metal hydroxide into oxide form accompanying with the crystal phase change from hexagonal to cubic. In the second step, the more enhancement arose from the greatly increased high crystallinity and the greatly reduced defects after high temperature annealing. Meanwhile, the size effect was not obvious because of the upconversion luminescence taking place from the emission centers.

The substantial enhancement in upconversion luminescence was also observed by using fluorescence spectrophotometer besides naked eyes as mentioned above (**Figure 4d**). For example, the calcined $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ at 1000 °C exhibited very strong upconversion luminescence, 4000× stronger than that of $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ prior to calcining. And the luminescence was 30× stronger than that of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ after treated at 600 °C by comparing their integrated areas in total. The decay kinetics of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ (**Figure S5**) were measured to show a great prolongation in luminescent lifetime with the increase of calcination temperature. The luminescent lifetime greatly increased at both 565 nm and 660 nm when varying the temperature from 600, 800 to 1000 °C, respectively, indicating the substantial enhancement in upconversion luminescence after treated at higher temperature (**Figure 4d**, **Figure S6**). Subsequently, the upconversion quantum yield of 1000 °C-calcined $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods was measured to be 1.6%, by using an FLS920 phosphorescence spectrometer equipped with an integrating sphere, comparable to those widely prepared upconversion nanoparticles like $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ or $\text{NaGdF}_4:\text{Yb}^{3+},\text{Er}^{3+}$.⁵⁵⁻⁵⁷

To optimize upconversion luminescence, the respective co-doping of Er^{3+} and Yb^{3+} ranging from 0.1-10 and 0-20 mol% was further performed to confirm the $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods with the strongest emission with a high green-to-red ratio (**Figure 5a**). Upon excitation, there are

three energy transfer processes including (a) energy transfer from sensitizer Yb^{3+} ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) to activator Er^{3+} ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$, $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$, $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$), (b) cross relaxation between Er^{3+} ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{9/2}$) and Er^{3+} ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$), and (c) energy back transfer from Er^{3+} ($^4\text{F}_{7/2} \rightarrow ^4\text{I}_{11/2}$) to Yb^{3+} ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$). Among them, the first process contributes to an effective upconversion luminescence in both green and red emissions, while the other two lead to a specific increase in red emission.⁵⁸⁻⁵⁹ For example, when retaining the level of Yb^{3+} at 10% but increasing the doping ratio of Er^{3+} from 1% to 2% or more, the cross relaxation between Er^{3+} was enhanced greatly to result in a higher red-to-green emission ratio (e.g. $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ for yellow emission and $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},5\%\text{Er}^{3+}$ for red emission). When retaining the level of Er^{3+} at 1% but decreasing the doping ratio of Yb^{3+} from 10% to a lower value, the energy back transfer from Er^{3+} to Yb^{3+} was reduced apparently while remaining a small cross relaxation between Er^{3+} to result in a higher green-to-red emission ratio (i.e. $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ with green emission).

The respective co-doping of Tm^{3+} and Yb^{3+} ranging from 0.1-2 and 0-20 mol% was also performed to obtain the $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},0.2\%\text{Tm}^{3+}$ rods with the strongest blue emission, of which the quantum yield was measured to be 0.34% (**Figure 5b**, **Figure S7**). Taken together with $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ system, a series of tunable emissions ranging from red, yellow, green to blue were generated to achieve multi-channel/deep bioimaging or color/white lighting through optimizing the use of different colors. When the $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ and the $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},0.2\%\text{Tm}^{3+}$ were mixed with different weight ratio (e.g. 0.4:1), a greenish upconversion luminescence was obtained by combining red, green and blue. When the $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ was used instead, a white-light upconversion luminescence was observed clearly (**Figure S8**) because of an adequate red-to-green ratio. For this combination, the upconversion white emission was greatly enhanced with the increased excitation power density

from 0.75 to 10 W/cm² (**Figure 5c**). The CIE chromaticity of emissions under various power densities (**Figure 5d**) showed that the combined Gd₂O₃:10%Yb³⁺,2%Er³⁺ and Gd₂O₃:10%Yb³⁺,0.2%Tm³⁺ phosphor was capable of generating white light emissions with a color temperature ranging from 3000 K to 8000 K.

To utilize the flexibility in tuning doping level to achieve different green-to-red ratio, Gd₂O₃:6%Yb³⁺,1%Er³⁺ nanorods (**Figure 6a**) were synthesized with very high green-to-red ratio (i.e. ~10:1 vs ~3:1 for Gd₂O₃:10%Yb³⁺,1%Er³⁺) with strong green emission for cellular imaging. To start with, CCD-112CoN cells were incubated with various concentrations of Gd₂O₃:Yb³⁺,Er³⁺ rods for 24 h. With the increase of concentration from 2, 5, 10, 25, 100 to 200 µg/mL, the cell viability slightly decreased but still maintained >90% upon incubation at 200 µg/mL (**Figure 6b**). Interestingly, as-prepared oxides were well-dispersed in aqueous solution with long-term stability without aggregation due to their respective positive surface charges of +26.5 mV (**Figure 6c,d**), facilitating direct interaction of nanorods with cells. For cellular imaging, CCD-112CoN cells (the nuclear counterstained with DAPI) were first grown on glass coverslips in a 96-well plate followed by washing and incubating with Gd₂O₃:Yb³⁺,Er³⁺ rods at 100 µg/mL for 4 h. After removing excessive rods with PBS, the confocal cellular image was collected from strong upconversion emission ranging from 510 to 560 nm (**Figure 6e**). The inset showed a three-dimensional overlay of confocal images at various depths, demonstrating the successful cellular uptake of Gd₂O₃:Yb³⁺,Er³⁺ nanorods. Benefiting from their very good chemical stability, Gd₂O₃:Ln³⁺ rods exhibit excellent optical stability in aqueous solutions and thus have more promise for bio-applications. Additionally, the ligand-free Gd₂O₃:Ln³⁺ nanorods with tunable luminescence capacities can be functionalized with various molecules including proteins for selective bioimaging and targeted therapeutics.

CONCLUSIONS

This paper demonstrated a flexible lanthanide co-loading of Yb³⁺, Er³⁺ and Tm³⁺ into Gd₂O₃ nanorods to obtain blue, green and red-dominant emissions for white light emissions and cellular imaging. A substantial enhancement in upconversion luminescence of Gd₂O₃:Yb³⁺,Er³⁺ nanorods was achieved by 30 times upon calcination at 1000 vs. 600 °C due to increased crystallinity, which was benefited from the complete transformation of hexagonal Gd(OH)₃:Yb³⁺,Er³⁺ to cubic Gd₂O₃:Yb³⁺,Er³⁺ at 600 °C and further crystallized at 1000 °C. Overall, this work provided a designation and understanding of efficient oxide-based upconversion nanomaterials, with a comparable quantum yield of 1.6% to those NaYF₄ or NaGdF₄-based upconversion ones. Also, the controlled surface charging in the absence of ligands or surfactants paves a way to offer self-dispersibility before/after thermal treatment for broader applications.

ASSOCIATED CONTENT

Supporting Information.

XRD patterns of as-prepared Gd(OH)₃ and Gd₂O₃ rods (Figure S1, S2); SAED patterns of Gd(OH)₃:10%Yb³⁺,1%Er³⁺ rods and 1000 °C-calcined Gd₂O₃:10%Yb³⁺,1%Er³⁺ rods (Figure S3); XRD patterns, FWHM comparison and emission decay kinetics of Gd₂O₃:10%Yb³⁺,1%Er³⁺ rods obtained by calcining at various temperature (Figure S4, S5); Emission spectra and energy transfer diagram of Gd₂O₃:Yb³⁺,Er³⁺ (Figure S6) and Gd₂O₃:Yb³⁺,Tm³⁺ (Figure S7); Emission spectra, digital images and CIE chromaticity diagram of phosphor assembled by Gd₂O₃:10%Yb³⁺,0.2%Tm³⁺ with Gd₂O₃:10%Yb³⁺,1%Er³⁺ or Gd₂O₃:10%Yb³⁺,2%Er³⁺ (Figure S8); Emission spectra and digital image of Gd₂O₃:6%Yb³⁺,1%Er³⁺ rods dispersed in aqueous

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3 solution. (Figure S9). These materials are available free of charge via the Internet at
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11 **AUTHOR INFORMATION**
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14 **Corresponding Author**
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16 *E-mail: ZLDong@ntu.edu.sg
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18

19 *E-mail: my-han@imre.a-star.edu.sg
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23 **Author Contributions**
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25 The manuscript was written through contributions of all authors. All authors have given approval
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33 **ORCID**
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36 ZhiLi Dong: 0000-0001-8116-6747
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39 Ming-Yong Han: 0000-0002-7519-6779
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43 **Notes**
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FIGURES

Figure 1. Surfactant-free hydrothermal synthesis of $\text{Gd}(\text{OH})_3$ rods in the presence of ammonia. (a) Schematic process for the hydrothermal synthesis of $\text{Gd}(\text{OH})_3$ rods. (b) Morphology evolution of $\text{Gd}(\text{OH})_3$ after synthesized with the use of various amount of ammonia. (c) Morphology evolution of $\text{Gd}(\text{OH})_3$ after synthesized at 80, 120 and 160 °C with 200 mM of ammonia by using TEM and SEM. (d) Titration curve of 10 mM Gd^{3+} solution with ammonia.

Figure 2. Mechanistic investigation for the formation of surface-charged Gd(OH)₃ rods through tuning size under different pH values. (a) TEM images of Gd(OH)₃ rods synthesized at various pH values ranging from pH 9.7, 10.0, 10.5, 11.0, 12.0 to 12.5 adjusted by adding 5M NaOH solution in the presence of 200 mM ammonia (Inset: a typical enlarged image of Gd(OH)₃ rods with a length of about 100 nm and a diameter of 12 nm. Scale bar: 20 nm). (b) Length and aspect ratio of Gd(OH)₃ rods as a function of pH values. (c) Dependence of zeta-potentials of mixtures immediately measured after prepared by adjusting pH of a mixture of 10 mM Gd³⁺ and 200 mM ammonia. The blue line represents the dependence of zeta-potentials of the purified Gd³⁺-ammonia dispersion by washing with water to pH~7 via centrifugation.

Figure 3. Systematic Yb³⁺-loading in Gd(OH)₃ rods and thermal transformation to Gd₂O₃:Yb³⁺. (a) XRD patterns of a series of Yb³⁺-loaded Gd(OH)₃ with various loading ratios (the maximum ratio of Yb/Gd = 3:7, or Gd(OH)₃:30%Yb³⁺). (b) SEM/EDX mapping of Gd(OH)₃:30%Yb³⁺, indicating homogeneous loading of Yb³⁺ in Gd(OH)₃. (c) XRD patterns of Yb³⁺-loaded Gd(OH)₃ after calcination into various structures at different temperatures. (d) TEM images of Gd(OH)₃:Yb³⁺ nanorods before and after calcination at 600 °C.

Figure 4. Co-doping of Yb³⁺ and Er³⁺ in Gd₂O₃ rods and substantial enhancement in upconversion of Gd(OH)₃:Yb³⁺,Er³⁺ rods. (a) Schematic illustration for Yb³⁺/Er³⁺ co-loading in Gd(OH)₃ to form Gd(OH)₃:Yb³⁺,Er³⁺ followed by compositional/structural transformation to Gd₂O₃:Yb³⁺,Er³⁺ rods with substantial enhancement in upconversion luminescence. (b) Low-resolution TEM images and SAED (selected area electron diffractions) of Gd(OH)₃:Yb³⁺,Er³⁺

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and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ after treated at 600 °C and 1000 °C (scale bar: 20 nm). (c) High-resolution TEM images and FFT of $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ after treated at 1000 °C (scale bar: 1 nm). (d) NIR-to-visible upconversion spectra of $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ treated at 600, 800 and 1000 °C. Right panel is the integral intensity of green/red emissions calculated from upconversion spectra, indicating a greatly enhanced upconversion luminescence of 1000 °C-calcined $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ versus the as-prepared $\text{Gd}(\text{OH})_3:\text{Yb}^{3+},\text{Er}^{3+}$ by 4000 times.

Figure 5. Systematic co-doping of Yb^{3+} and Er^{3+} or Tm^{3+} in Gd_2O_3 for white-light upconversion luminescence through a combined blue, green and red emission. (a) Upconversion spectra for demonstrating optimized co-doping of Yb^{3+} and Er^{3+} with various doping ratios in Gd_2O_3 to generate green and red emission. (b) Upconversion spectra for demonstrating optimized co-loading of Yb^{3+} and Tm^{3+} in Gd_2O_3 with various doping ratios to generate blue emission. (c) Upconversion spectra of $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ and $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+},0.2\%\text{Tm}^{3+}$ optimized at (a) and (b) under various power densities of 980 nm laser. (d) CIE chromaticity diagram of white light phosphor under various excitation power density.

Figure 6. $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods with excellent aqueous dispersibility for cellular imaging. (a) TEM image of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods after thermal calcination of $\text{Gd}(\text{OH})_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ at 1000 °C. (b) Cell viability of CCD-112CoN cells incubated with various concentrations of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods for 24 h. (c) Zeta-potential of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods in water. (d) Upconversion luminescence image of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods in water. (e) Confocal upconversion image for the cellular uptake of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods by CCD-112CoN cells with DAPI-stained nucleus. Insert is the 3D images at various depths, indicative of the successful uptake of $\text{Gd}_2\text{O}_3:6\%\text{Yb}^{3+},1\%\text{Er}^{3+}$ rods by CCD-112CoN cells.

Table of Contents Graphic