Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsC

Journal of Materials Chemistry C

Pure near-infrared to near-infrared upconversion and paramagnetism were observed in $NaGd(WO_4)_2$: Tm^{3+} , Yb^{3+} nanoparticles, suggesting they are promising for applications in high-contrast bio-imaging and bio-separation.



Pure Near-Infrared to Near-Infrared Upconversion of Multifunctional Tm³⁺ and Yb³⁺ Co-Doped NaGd(WO₄)₂ Nanoparticles

Zhaofeng Wang,^a Yezhou Li,^a Qi Jiang,^b Huidan Zeng,^{b,*} Zhipeng Ci^c and Luyi Sun^{a,*}

^aDepartment of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States ^bKey Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

^cDepartment of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, China

*Authors to whom correspondence should be addressed:

Dr. Luyi Sun, Tel: (860) 486-6895; Fax: (860) 486-4745; Email: luyi.sun@uconn.edu

Dr. Huidan Zeng, Tel/Fax: 8621 64253395; Email: hdzeng@ecust.edu.cn

Journal of Materials Chemistry C Accepted Manuscript

Abstract

In this work, Tm^{3+} and Yb^{3+} co-doped NaGd(WO₄)₂ nanoparticles were synthesized via surfactant-assisted hydrothermal reactions. The structure analysis indicates that Tm^{3+} and Yb^{3+} ions have been doped into NaGd(WO₄)₂ host by occupying the sites of Gd³⁺. The as-prepared NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} nanomaterials are spherical particles with an approximate size of 50-80 nm. The upconversion spectra results suggest that NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} nanoparticles exhibit pure or virtually pure near-infrared to near-infrared upconversion luminescence when excited by a 975 nm laser. This phenomenon is significant for the nanoparticles to be applied in bio-imaging, because both the excitation and emission in near-infrared region will reduce the autofluorescence and light scattering from the biological tissues. On the basis of the upconversion emission is proposed. Moreover, the NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} nanoparticles also exhibit paramagnetism, promising for bio-separation.

Keywords: Near-infrared to near infrared, Upconversion, Nanoparticles, Magnetic properties

Journal of Materials Chemistry C Accepted Manuscript

Introduction

Upconversion (UC) is a process in which low energy photons, usually near-infrared (NIR) or infrared (IR), are converted to high energy photons via multiple absorptions or energy transfers.¹⁻⁵ UC luminescence materials have been broadly investigated for diverse applications, such as displays, lasers, backlight, and alternatives to general lighting.^{4, 6, 7}

During the past several years, low-dimensional UC nanoparticles (UCNPs) have received considerable attention for their underlying scientific applications, especially in the field of bio-technology, e.g., biological labels and imaging.⁸⁻¹³ This is because the excitation source of UCNPs usually adopt NIR radiation, and biological tissues have a minimum light absorption coefficient in NIR region (750~1000 nm).¹⁴⁻¹⁷ For ultraviolet (UV) and visible (Vis) light, they are easily be absorbed by biological tissues leading to autofluorescence, which interferes with fluorescent signals obtained from exogenous.^{12, 18} Moreover, the penetration of NIR radiation is deeper than that of UV and visible light. For example, NIR can travel at least 10 cm through breast tissue, and 4 cm of skull/brain tissue or deep muscle using microwatt laser sources.^{4, 14, 19} However, most of the present researches have been focusing on the conversion of near-infrared light to visible light using rare earth ions doped nanomaterials.²⁰⁻²³ Therefore, it is desirable to explore UCNPs with both excitation and emission in the NIR region for in vitro and in vivo imaging applications. By use of such UCNPs for bio-imaging, autofluorescence and light scattering from the biological tissues would be reduced with increasing image contrast.

Recently, several research groups have explored NIR-NIR UCNPs for biological applications and obtained promising results.^{18, 19, 24-29} The UCNPs in their researches were

mainly Tm³⁺ and Yb³⁺ co-doped fluoride nanoparticles. Prasad and coworkers¹⁸ reported an approach for high contrast in vitro and in vivo photoluminescence bio-imaging by use of NaYF₄: Tm³⁺, Yb³⁺ UCNPs. The UCNPs exhibited main emission around 800 nm in NIR region when excited by a 975 nm laser. In order to be used as bio-imaging probes more efficiently, they further adopted a modified cothermolysis method to prepare monodisperse NaYF₄: Tm³⁺, Yb³⁺ nanocrystals of ultrafine size (7-10 nm), in which high NIR to NIR UC efficiency were produced.²⁴ Wong et al. synthesized KGdF₄: Tm³⁺, Yb³⁺ and GdF₃: Tm³⁺, Yb³⁺ UCNPs.^{19, 26} They found that both UCNPs exhibited intense NIR to NIR UC luminescence, indicating that they were suitable for biological applications. Although the strong NIR UC emission is demonstrated in the above materials, considerable impurity emissions (most are blue and red lights originated from ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ (${}^{3}F_{4}$) and ${}^{3}F_{3} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺) still exist in these UCNPs, especially for NaYF₄: Tm³⁺, Yb³⁺. These stray lights directly influence the quality of the photoluminescence bio-imaging. The urgent need in bio-imaging for more effective diagnosis motivates researchers to explore novel UCNPs with pure NIR to NIR UC luminescence.

The pioneering work in this field as discussed above^{18, 19, 24-29} has suggested that the ratio of the intensity of NIR emission to visible light can be varied in a wide range by utilizing different matrices, although the activation ions and the doping concentration remain the same. This inspires us to explore potentially pure NIR to NIR UC by doping Tm^{3+} and Yb^{3+} in an appropriate matrix. In this work, we demonstrated that $NaGd(WO_4)_2$ was such an excellent host. It is a scheelite-like double tungstate with excellent thermal, hydrolytic, and chemical stability.³⁰⁻³² NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} UCNPs were synthesized by a facile

Journal of Materials Chemistry C Accepted Manuscript

surfactant-assisted hydrothermal route. Upon the irradiation of a 975 nm laser, most of the UCNPs present pure NIR emission band at ~800 nm. Possible physical mechanisms related to the activation ions and host were discussed by analyzing the UC and Raman spectra. Furthermore, the Tm^{3+} and Yb^{3+} co-doped NaGd(WO₄)₂ UCNPs were found to possess paramagnetism. The multifunctional UCNPs with pure NIR to NIR UC luminescence and magnetic properties are of great significance for applications in high-contrast bio-imaging and bio-separation.

Experimental

Materials

Na₂WO₄·2H₂O (>99%), and Gd(NO₃)₃·6H₂O (99.9%) were purchased from Acros Organics. Tm₂O₃ (99.99%) and Yb₂O₃ (99.99%) were obtained from Alfa Aesar. Cetyltrimethylammonium bromide (CTAB, >99%) and nitric acid (65%) were purchased from Amersco, Inc. All the raw materials were used as received.

Synthesis

NaGd_{0.9-x}(WO₄)₂: xTm³⁺, 0.1Yb³⁺ UCNPs were prepared via surfactant-assisted hydrothermal reactions. First, 0.375x mmol Tm₂O₃ and 0.0375 mmol Yb₂O₃ were dissolved in dilute nitric acid under heating. After they were completely dissolved, the excess nitric acid was removed by evaporation, and 32 mL of deionized water was added to obtain a solution with a pH value of ~6. Then, 0.10 g surfactant CTAB and $0.75 \times (0.9-x)$ mmol Gd(NO₃)₃·6H₂O were added to the solution with continuous stirring at 60 °C. Subsequently, 1.5 mmol Na₂WO₄·2H₂O was added, which was accompanied by the appearance of aqueous emulsion. After stirring for 2 h

at 60 °C, the emulsion was transferred into a Teflon-lined stainless steel autoclave and heated to 150 °C for 10 h. Then the autoclave was cooled to room temperature naturally and the product was washed and collected by vacuum filtration using water and ethanol. After drying in a vacuum oven at room temperature for 12 h, the final product was obtained. The yield of the UCNPs was ~95%.

Characterization

The crystal phase of the obtained materials was characterized by X-ray diffraction (XRD, Bruker D8, 40 kV and 30 mA) using a graphite monochromator with Cu K α radiation (λ = 0.1540 nm). The morphology and microstructure of the prepared UCNPs were characterized by scanning electron microscopy (SEM, FEI Helios Nanolab 400, operated at 10 kV). The Energy Dispersive Spectrometer (EDS) was the affiliated instrument of SEM. Raman spectroscopy (Thermo Scientific, DXR, 532 nm laser) was employed to characterize the structural and electronic properties of the samples. The optical absorption of the samples was measured by a UV-Vis-NIR spectrophotometer (CARY 500, Varian Company). The UC luminescence spectra were recorded at room temperature on an Edinburgh FLS920P spectrometer, excited by a power tunable 1550 nm semiconductor laser diode (0~500 mW). The measurements of magnetic properties were conducted on a vibrating sample magnetometer (VSM, Lakeshore 7304 series). All the characterizations were performed at room temperature.

Results and discussion

NaGd(WO₄)₂ crystal belongs to the scheelite-like structure with the space group of I41/a.³³

Fig. 1a shows the typical XRD patterns of the prepared NaGd(WO₄)₂ nanoparticles with and without doping of Tm^{3+} and Yb^{3+} . It was observed from the patterns that all diffraction peaks of the samples synthesized by CTAB-assisted hydrothermal reaction can be indexed and match well with the standard data of scheelite phase NaGd(WO₄)₂ (JCPDs card no. 25-0829). This indicates that single phase $NaGd(WO_4)_2$ crystals were obtained and meanwhile no traces of additional peaks corresponding to other phases aroused by doping of Tm^{3+} and Yb^{3+} were observed. In the host of NaGd(WO₄)₂, there are two possibilities for Tm^{3+} and Yb^{3+} to be doped. One is the substitution of Gd^{3+} . As the radii of Tm^{3+} and Yb^{3+} ions are both slightly smaller than that of Gd³⁺, this substitution would induce host lattice shrinking. The other doping approach is that Tm³⁺ and Yb³⁺ ions could occupy the interstitial sites, leading to the expansion of the crystal lattice. To identify the approach of doping Tm³⁺ and Yb³⁺ in NaGd(WO₄)₂, the magnified curves of (112) diffraction peak of the samples are shown in Fig. 1b. It is found that the position of the peak consistently shifts to higher degree, and the shift is more significant with an increasing concentration of dopant. According to the Bragg equation, such a shift should be aroused by the reduction of the lattice distance (d). This result confirms that both Tm³⁺ and Yb³⁺ have been successfully doped through occupying the sites of Gd³⁺.



Fig. 1 (a) XRD patterns of NaGd(WO₄)₂ nanoparticles with and without doping of Tm³⁺ and Yb³⁺;
(b) Evolution of the shift of (112) peak magnified from (a).

The microstructure and morphology of the as-made NaGd(WO₄)₂: Tm³⁺, Yb³⁺ nanoparticles were revealed by SEM. The UCNPs were dispersed in ethanol by ultrasonication. The obtained dispersion was then dipped on the surface of conductive adhesive for morphology characterization. Fig. 2 displays the representative SEM micrographs of NaGd(WO₄)₂: 1%Tm³⁺, 10%Yb³⁺ UCNPs at different magnifications and the corresponding EDS spectrum. From Fig. 2a-c, one can observe that the obtained material is composed of nanoparticles with a size of 50~80 nm. Generally, the use of nitrates as raw materials during hydrothermal processes will lead to a fast growth rate of NaGd(WO₄)₂ crystals, preferring to form micro-sized octahedral crystals.³⁰ The nano-meter sized UCNPs as observed in Fig. 2a-c should be ascribed to the functions of surfactant CTAB. On one hand, the addition of CTAB in an aqueous solution will effectively reduce its surface energy,³⁴ leading to a better dispersibility of the crystalline seeds. Hence, the aggregation of NaGd(WO₄)₂ crystals will be prevented to some extent during the subsequent hydrothermal treatment. On the other hand, due to the electrostatic interaction between cations (CTA⁺) and

anion group (WO_4^{2-}) , CTA⁺ cations could absorb on the surface of NaGd $(WO_4)_2$ crystals, limiting their further growth into large particles.³⁵

The corresponding EDS spectrum of the UCNPs in the region of Fig. 2b suggests that the nanoparticles are mainly composed of the elements of Na, Gd, W, O, and Yb (C and Cu are originated from the conducting adhesive). The element of Tm was not clearly detected, which is believed owing to its very low doping concentration (only 1 at.%).



Fig. 2 (a-c) SEM micrographs of NaGd(WO₄)₂: 1%Tm, 10%Yb nanophosphor under different magnifications; (d) the corresponding EDS spectrum of UCNPs in (b).

To investigate the influence of Tm^{3+} and Yb^{3+} on the luminescence properties of UCNPs, the absorption spectra in the UV-Vis-NIR region at room temperature were measured. Fig. 3 shows the UV-Vis-NIR absorption spectra of NaGd(WO₄)₂ matrix, NaGd(WO₄)₂: 1%Tm³⁺, and NaGd(WO₄)₂: 1%Tm³⁺, 10%Yb³⁺. For the host of NaGd(WO₄)₂, only one absorption band around 260 nm was observed, attributing to the electronic transition from oxygen 2p state to tungsten 5d state in WO₄^{2-,36,37} When the introduction of Tm³⁺ ions in the sites of Gd³⁺, an additional peak at ~683 nm arises which could be assigned to the ${}^{3}H_{6} \rightarrow {}^{3}F_{3}$ transition of Tm³⁺ (clearly shown in the inset of Fig. 3).^{38,39} With further co-doping of Yb³⁺, a broad absorption band ascribing to the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition of Yb³⁺ appears at around 975 nm.⁴⁰ The full-width at half-maximum (FWHM) of the absorption band reaches 73.8 nm, suggesting that NaGd(WO₄)₂: Tm³⁺, Yb³⁺ UCNPs can be efficiently pumped by a 975 nm laser. It is also found that the locations of charge transfer transition in WO₄²⁻ shift to shorter wavelengths (from 260 nm to 258 and 251 nm) with an increasing doping concentration, which could be related to the slight crystal lattice distortion caused by the substitution of Tm³⁺ and Yb³⁺ to Gd³⁺.



Fig. 3 UV-Vis-NIR spectra of NaGd(WO₄)₂, NaGd(WO₄)₂: 1%Tm, and NaGd(WO₄)₂: 1%Tm,

10%Yb. The inset exhibits the magnified region from 400 to 750 nm.

The UC spectra of NaGd(WO₄)₂: Tm³⁺, Yb³⁺ UCNPs series under 975 nm laser excitation are shown in Fig. 4a. For NaGd(WO₄)₂: x%Tm, 10%Yb UCNPs with x = 0.2, 1 and 2, pure NIR emission around 800 nm are observed without any visible light. The NIR

emission can be ascribed to the characterized ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition of Tm^{3+,24} When the doping concentration of Tm^{3+} is 0.5%, a weak peak appears at ~475 nm, corresponding to the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ electron transition of Tm³⁺ as shown in the inset of Fig. 4a.⁴¹ Even so, the integrated intensity ratio of the NIR emission to visible light still reaches ~20. The reason for the generation of pure NIR to NIR UC emission in NaGd(WO₄)₂: x%Tm³⁺, 10%Yb³⁺ UCNPs (x=0.2, 1, 2) and the appearance of the weak blue light in NaGd(WO₄)₂: 0.5%Tm³⁺, 10%Yb³⁺ UCNPs will be discussed in detail in the next section. From Fig. 4a, it is also found that the UC photoluminescence intensity of the UCNPs is greatly affected by the doping concentration of Tm^{3+} . The most intense NIR emission is observed in NaGd(WO₄)₂: $x\%Tm^{3+}$, 10%Yb³⁺ UCNPs (x=0.5), while the intensity decreases at a content of x=1, 2. This variation of the photoluminescence intensity on dependence of doping concentration is caused by the concentration quenching.⁴² It should be noted that NaGd(WO₄)₂: 1%Tm³⁺, 10% Yb³⁺ nanoparticles exhibit a very close NIR upconversion intensity to that of NaYF₄: 1%Tm³⁺, 10% Yb³⁺ micro-hexagonal prisms that contain obvious blue emission in upconversion spectrum. Hence, NaGd(WO₄)₂: 1%Tm³⁺, 10% Yb³⁺ nanoparticles with strong and pure NIR to NIR upconversion are promising for high-contrast bio-imaging applications.

Fig. 4b exhibits the comparison of the UC spectra of NaGd(WO₄)₂: 1%Tm³⁺, 10%Yb³⁺ UCNPs under the pump current from 1.0 to 2.0 mA. The NIR emission intensity of the UCNPs enhances dramatically with an increasing pump current. By converting the current to pump power, the dependence of UC intensity on the power of excitation was obtained. Fig. 4c shows the log-log plots of the NIR UC emission intensities (${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ of Tm³⁺) of NaGd(WO₄)₂: *x*Tm, 10%Yb (x=0.002, 0.005, 0.01 and 0.02) UCNPs as a function of the 975

Journal of Materials Chemistry C

nm excitation power. Generally, the number of photons which are required to populate the upper emitting state under unsaturated conditions can be obtained by the relation:¹

$$I_f \propto P^n$$
 (1)

where I_f , P, and n represents photoluminescence intensity, pump laser power, and number of the laser photons required, respectively. As can be seen in Fig. 4c, all slope values are in the range of 1.56~1.73, illustrating that two photon processes were involved to generate the NIR to NIR UC.

The UC pathways of Yb³⁺ and Tm³⁺ ions under the excitation of 975 nm radiation have been proposed in many hosts.^{9, 10, 41, 43} Generally, NIR and visible UC luminescence of Yb³⁺ and Tm³⁺ ions are corresponding to two-photon and three-photon processes, respectively. In our case, the NIR to NIR UC mechanism of NaGd(WO₄)₂: Tm³⁺, Yb³⁺ should be similar to the common one (two-photon processes). The absent or weak visible UC emission in NaGd(WO₄)₂: Tm³⁺, Yb³⁺ UCNPs indicates that the third photon UC process from Yb³⁺ to Tm^{3+} ions to excite electrons from ${}^{3}H_{4}$ to ${}^{1}G_{4}$ state is effectively prevented. The previous studies indicated that the relative intensity ratio of visible to NIR upconversion emission of Tm³⁺ could be achieved by varying the doping concentration and controlling the particle size.^{3,44} However, it is found in this work that the concentration of Tm³⁺ has little influence on the intensity ratio of visible to NIR upconversion emission. Additionally, the NIR to visible ratio is far higher than those in other hosts (e.g. LaF3⁴⁵) with a same doping concentration (1%Tm³⁺ and 10% Yb³⁺) and similar particle size (~50 nm). This suggests that NaGd(WO₄)₂ host should be responsible for the pure or virtually pure NIR upconversion. As the energy transfer from Yb³⁺ to Tm³⁺ ions is believed to be assisted by phonons of the host,⁴⁶

a possible UC mechanism associated with the phonon-assisted energy transfer (PAET) process for NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} UCNPs is proposed and illustrated in Fig. 4d.



Fig. 4 (a) Upconversion luminescence spectra of NaGd(WO₄)₂: x%Tm, 10%Yb UCNPs with x varies from 0.2 to 2 at the pump current of 1.8 mA; (b) Upconversion luminescence spectra of NaGd(WO₄)₂: 1%Tm, 10%Yb UCNPs under the pump current from 1.0 to 2.0 mA (λ_{ex} =975 nm); (c) Log-log plots of the NIR UC emission intensities (${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ of Tm³⁺) of NaGd(WO₄)₂: xTm, 10%Yb (x=0.002, 0.005, 0.01 and 0.02) UCNPs as a function of the 975 nm excitation power; (d) Phonon-assisted UC luminescence mechanism of Tm³⁺, Yb³⁺ co-doped UCNPs.

In order to verify the UC mechanism, Raman spectrum of NaGd(WO₄)₂ host was

Journal of Materials Chemistry C

acquired and is shown in Fig. 5. The locations of the ${}^{1}G_{4}$, ${}^{3}F_{3}$ and ${}^{3}H_{4}$ energy levels of Tm³⁺ and ²F_{5/2} level of Yb³⁺ in NaGd(WO₄)₂: Tm³⁺, Yb³⁺ nanoparticles could be accurately calculated from the absorption and upconversion spectra. These locations agree well with the previous reports.⁴⁷⁻⁴⁹ By combining the results from our work and their work, all locations for energy levels of Tm^{3+} and Yb^{3+} are estimated. As a result, the energy mismatches between the transitions within the Yb³⁺ (${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$) and the Tm³⁺ (${}^{3}H_{6} \rightarrow {}^{3}H_{5}$, ${}^{3}F_{4} \rightarrow {}^{3}F_{2}$, ${}^{3}H_{4} \rightarrow {}^{1}G_{4}$) are estimated to be 1840, 995 and 1651 cm⁻¹, respectively. The phonon modes with energies around 917.9 and 330.5 cm⁻¹ are responsible for the PAET rates from Yb³⁺ to Tm³⁺ ions. For the processes of PAET1 and PAET2, only two phonons with an energy of 917.9 cm⁻¹ and three phonons with an energy around 330.5 cm⁻¹ for NaGd(WO₄)₂ host are required to fill up the energy mismatch. However, to fill up the energy mismatch of the ${}^{3}H_{4} \rightarrow {}^{1}G_{4}$ transition (1651 cm⁻¹) during PAET3, five phonons with an energy of 330.5 cm⁻¹ are needed. The much higher number of phonons of the latter suggests that the electron at the excited state of ${}^{3}H_{4}$ is more likely to recombine with holes by emitting NIR light, instead of being further excited to ¹G₄ energy level to generate visible emissions.¹⁹ Hence, the restriction of PAET3 from Yb³⁺ to Tm^{3+} by NaGd(WO₄)₂ host is believed to be the key reason for the generation of pure or nearly pure NIR UC photoluminescence.

With an aim to further confirm the proposed PAET mechanism, some Raman and upconversion results of Tm^{3+} and Yb^{3+} co-doped samples are summarized from references.^{19, 24, 43, 50-54} It is found that this mechanism is also suitable for many other matrices co-doped by Tm^{3+} , Yb^{3+} . Herein, GdF_3 , YF_3 , Bi_5O_7I , YVO_4 and $NaYF_4$ hosts are presented as representative examples. For GdF_3 : Tm^{3+} , Yb^{3+} , all samples exhibit nearly pure NIR to NIR

upconversion although the concentration of Tm³⁺ varies (from 0.5 to 3 mol%).¹⁹ It is calculated that five phonons at $\sim 360 \text{ cm}^{-1}$ in GdF₃ host are required to fill up the energy mismatch for the processes of PAET3. Therefore, the PAET3 process is efficiently prevented, resulting in the high ratio of NIR to visible emissions. For YF₃: Tm³⁺, Yb³⁺, the ratio of NIR to visible emissions is lower compared with that of GdF_3 : Tm^{3+} , Yb^{3+} .¹⁹ This is because less phonons (four phonons at ~450 cm⁻¹) in YF₃ is needed to fill up the energy mismatch. Li et al.⁵⁰ reported that Bi₅O₇I: Tm³⁺, Yb³⁺ exhibits nearly pure NIR to NIR upconversion. Based on the calculation from the Raman spectrum of Bi_5O_7I host, five phonons with an energy at ~335 cm⁻¹ are needed for PAET3. These results from Tm^{3+} , Yb^{3+} co-doped YF₃, GdF₃ and Bi₅O₇I agree well with the discussion in our work. It indicates that the visible emission would be efficiently limited if the required number of phonons for PAET3 is five or more, and this phenomenon will not be changed even by varying the doping concentration. For YVO₄: Tm³⁺, Yb³⁺, Hazra et al.⁵¹ reported that the intensity of the blue upconversion peak was nearly as strong as that of NIR emission. The Raman spectrum in Basiev's work⁵² indicated that the phonons at \sim 820 cm⁻¹ should participate in the process of PAET3, in which only two phonons are needed to fill up the mismatch, which is beneficial to achieve the visible emission. This result also supports the PAET upconversion mechanism in our work.

It is interesting to find that NaYF₄: Tm^{3+} , Yb^{3+} could exhibit upconversion emission with different NIR/Vis ratios with the doping concentration remains the same. For example, Chen et al.²⁴ reported that NaYF₄: 2%Tm³⁺, 20%Yb³⁺ ultrafine nanoparticles (~ 8 nm) showed a strong NIR upconversion emission with a very low proportion of visible emission. However, Boyer et al.⁴³ reported that NaYF₄: 2%Tm³⁺, 20%Yb³⁺ with large particle size showed an

obvious blue emission besides the NIR light. Obviously, this phenomenon should be attributed to the different particle size, which can be well explained by the PAET mechanism. Suyver et al.⁵³ reported Raman characterization of NaYF₄ powders, in which three dominant phonon modes were found to be 298, 370 and 418 cm⁻¹. So, it can be concluded that four phonons with an energy of ca. 418 cm⁻¹ are required to fill up the energy mismatch for PAET3 in NaYF₄: Tm³⁺, Yb³⁺ powder (large particle size). However, things are different for the NaYF₄: Tm³⁺, Yb³⁺ ultrafine nanoparticles (~8 nm). When the particle size reduced to be less than 10 nm, significant red Raman shift would occur and the phonons with an energy of ca. 355 cm⁻¹ in the ultrafine NaYF₄ host will assist the energy transfer from ${}^{2}F_{5/2}$ of Yb³⁺ to ${}^{1}G_{4}$ of Tm³⁺.⁵⁴ Therefore, the required number of phonons for PAET3 should be five in NaYF₄: Tm³⁺, Yb³⁺ ultrafine nanoparticles. This explains why NaYF₄: 2%Tm³⁺, 20%Yb³⁺ samples with different particle sizes exhibit different NIR to visible emission ratios.



Fig. 5 Room temperature Raman spectrum of NaGd(WO₄)₂ matrix excited at 532 nm.

Although most of the NaGd(WO₄)₂ based UCNPs exhibit pure NIR UC emission, a weak visible emission located at about 475 nm was observed in the samples under high pump

current (2.0 mA) and in the sample containing 0.5% dopant of Tm³⁺, as shown in the insets of Fig. 4a-b. In other words, a little visible light will be generated in the samples with the most intense NIR UC emission. To interpret this phenomenon, the following steady-state equations from the energy diagrams are utilized:^{1, 24}

$$N_2 N_{Yb1} W_3 - N_3 R_3 = 0$$
 (2)
 $N_{Yb1} = \rho \sigma N_{Yb0}$ (3)

$$I_f = N_3 h \nu_{Vis} R_3 \tag{4}$$

Where N_{Yb0} , N_{Yb1} , N_2 , and N_3 are the population density of the ${}^2F_{7/2}$ (Yb³⁺), ${}^2F_{5/2}$ (Yb³⁺), 3H_4 (Tm³⁺), and 1G_4 (Tm³⁺) states, respectively; W_3 is the energy transfer rate from the excited Yb³⁺ ions to 3H_4 state of Tm³⁺ ions; R_3 is radiative rate of 3H_4 state of Tm³⁺ ions; ρ represents the laser photon number density; σ is the absorption cross-section of the Yb³⁺ ions; I_f denotes the intensity of visible UC emission; v_{Vis} is the frequency of visible light; and h is the Planck constant. Thus, from equations (2-4), the intensity of the visible UC emission can be expressed as:

$$I_f = N_2 N_{Yb0} W_3 \rho \sigma h \nu_{Vis} \tag{5}$$

Therefore, although W_3 is restricted to some extent by NaGd(WO₄)₂ host, the most intense NIR emission corresponding to a large value of N_2 will still arouse the appearance of the weak visible emission.

In addition to the pure NIR to NIR UC performance, the magnetic properties of NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} UCNPs were also investigated. Fig. 6 shows the magnetization of NaGd(WO₄)₂ host and NaGd(WO₄)₂: $1\%Tm^{3+}$, $10\%Yb^{3+}$ as a function of applied magnetic field. The linear correlation as shown in Fig. 6 suggests that both materials possess

paramagnetism.^{9, 19} The mass magnetic susceptibility value of NaGd(WO₄)₂ was measured to be 4.43×10^{-5} emu/g·Oe, and the magnetization at 10 kOe was around 0.443 emu/g. The paramagnetic properties of NaGd(WO₄)₂ are from the Gd³⁺ ions, which has been discussed in detail in the literature.^{55, 56} There is only a slight influence on the magnetic properties of the NaGd(WO₄)₂ nanoparticles after doping Tm³⁺ and Yb³⁺ ions, and the magnetization of NaGd(WO₄)₂: 1%Tm³⁺, 10%Yb³⁺ UCNPs at 10 kOe is determined to be 0.418 emu/g. The multifunctional NaGd(WO₄)₂: Tm³⁺, Yb³⁺ UCNPs with pure NIR to NIR UC and magnetic properties present potential applications in high-contrast in vitro and in vivo bio-imaging and bio-separation.



Fig. 6 Magnetization as a function of the applied magnetic field of $NaGd(WO_4)_2$ host and $NaGd(WO_4)_2$: 1%Tm³⁺, 10%Yb³⁺ UCNPs at room temperature.

Conclusions

 $NaGd(WO_4)_2$: Tm^{3+} , Yb^{3+} UCNPs have been successfully synthesized via a CTAB-assisted hydrothermal approach. The UCNPs were observed to present pure or virtually pure NIR to NIR upconversion. By fitting the log-log plot of the NIR UC emission intensities of the UCNPs as a function of the 975 nm excitation power, two photon processes were confirmed. On the basis of analyzing the phonon modes from Raman spectrum and the mismatch energy between the energy levels of Yb^{3+} and Tm^{3+} , the UC mechanism for the generation of pure or virtually pure NIR emission in NaGd(WO₄)₂: Tm^{3+} , Yb^{3+} was proposed, which is also found to be suitable for many other systems. In addition to the excellent UC properties, the NaGd(WO₄)₂ based UCNPs also possess paramagnetism, suggesting that they are promising for applications in high-contrast bio-imaging and bio-separation.

Acknowledgements

This research is sponsored by the National Science Foundation (Partnerships for Research and Education in Materials, DMR-1205670), the Air Force Office of Scientific Research (No. FA9550-12-1-0159), and the Faculty Large Grant from the University of Connecticut.

References

- 1. M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel and M. P. Hehlen, *Physical Review B*, 2000, **61**, 3337-3346.
- 2. F. Auzel, *Chemical reviews*, 2004, **104**, 139-174.
- 3. F. Wang and X. Liu, *Journal of the American Chemical Society*, 2008, **130**, 5642-5643.
- 4. F. Wang and X. Liu, *Chemical Society Reviews*, 2009, **38**, 976-989.
- F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong and X. Liu, *Nature*, 2010, 463, 1061-1065.

- 6. V. Mahalingam, F. Mangiarini, F. Vetrone, V. Venkatramu, M. Bettinelli, A. Speghini and J. A. Capobianco, *The Journal of Physical Chemistry C*, 2008, **112**, 17745-17749.
- C. Liu, H. Wang, X. Zhang and D. Chen, *Journal of Materials Chemistry*, 2009, 19, 489-496.
- 8. D. K. Chatterjee, A. J. Rufaihah and Y. Zhang, *Biomaterials*, 2008, 29, 937-943.
- 9. G.-S. Yi and G.-M. Chow, *Chemistry of Materials*, 2007, **19**, 341-343.
- 10. G.-S. Yi and G.-M. Chow, *Journal of Materials Chemistry*, 2005, **15**, 4460-4464.
- N. Bogdan, E. M. Rodríguez, F. Sanz-Rodríguez, M. C. I. de la Cruz, Á. Juarranz, D. Jaque, J. G. Solé and J. A. Capobianco, *Nanoscale*, 2012, 4, 3647-3650.
- 12. F. Wang, D. Banerjee, Y. Liu, X. Chen and X. Liu, *Analyst*, 2010, **135**, 1839-1854.
- J. Wang, F. Wang, C. Wang, Z. Liu and X. Liu, Angewandte Chemie, 2011, 123, 10553-10556.
- 14. R. Weissleder, *Nature Biotechnology*, 2001, **19**, 316-317.
- C. T. Xu, N. Svensson, J. Axelsson, P. Svenmarker, G. Somesfalean, G. Chen, H. Liang, H. Liu, Z. Zhang and S. Andersson-Engels, *Applied Physics Letters*, 2008, 93, 171103-171103-171103.
- S. Heer, K. Kömpe, H. U. Güdel and M. Haase, Advanced Materials, 2004, 16, 2102-2105.
- 17. Z. Li and Y. Zhang, Angewandte Chemie, 2006, 118, 7896-7899.
- M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey and P. N. Prasad, *Nano letters*, 2008, 8, 3834-3838.
- 19. H.-T. Wong, H. L. Chan and J. Hao, *Optics express*, 2010, **18**, 6123-6130.

- 20. H. Guo, N. Dong, M. Yin, W. Zhang, L. Lou and S. Xia, *The Journal of Physical Chemistry B*, 2004, **108**, 19205-19209.
- F. Vetrone, J.-C. Boyer, J. A. Capobianco, A. Speghini and M. Bettinelli, *Chemistry of Materials*, 2003, 15, 2737-2743.
- Y. Sun, H. Liu, X. Wang, X. Kong and H. Zhang, *Chemistry of Materials*, 2006, 18, 2726-2732.
- S. Jiang, Y. Zhang, K. M. Lim, E. K. Sim and L. Ye, *Nanotechnology*, 2009, 20, 155101.
- 24. G. Chen, T. Y. Ohulchanskyy, R. Kumar, H. Ågren and P. N. Prasad, *ACS nano*, 2010,
 4, 3163-3168.
- G. Chen, T. Y. Ohulchanskyy, W. C. Law, H. Ågren and P. N. Prasad, *Nanoscale*, 2011, 3, 2003-2008.
- H.-T. Wong, F. Vetrone, R. Naccache, H. L. W. Chan, J. Hao and J. A. Capobianco, Journal of Materials Chemistry, 2011, 21, 16589-16596.
- J. Zhou, Y. Sun, X. Du, L. Xiong, H. Hu and F. Li, *Biomaterials*, 2010, 31, 3287-3295.
- N.-N. Dong, M. Pedroni, F. Piccinelli, G. Conti, A. Sbarbati, J. E. Ramírez-Hernández, L. M. n. Maestro, M. C. Iglesias-de la Cruz, F. Sanz-Rodriguez and A. Juarranz, ACS nano, 2011, 5, 8665-8671.
- G. Chen, J. Shen, T. Y. Ohulchanskyy, N. J. Patel, A. Kutikov, Z. Li, J. Song, R. K.
 Pandey, H. Ågren and P. N. Prasad, ACS nano, 2012, 6, 8280-8287.
- 30. F. Esteban-Betegón, C. Zaldo and C. Cascales, Chemistry of Materials, 2010, 22,

2315-2324.

- 31. B. Yan, L. Lin, J. Wu and F. Lei, *Journal of fluorescence*, 2011, **21**, 203-211.
- 32. H. Wang, C. Tu, Z. You, F. Yang, Y. Wei, Y. Wang, J. Li, Z. Zhu, G. Jia and X. Lu, *Applied Physics B*, 2007, **88**, 57-60.
- J. Fan, H. Zhang, J. Wang, Z. Ling, H. Xia, X. Chen, Y. Yu, Q. Lu and M. Jiang, Journal of Physics D: Applied Physics, 2006, 39, 1034.
- Z. Wang, J. Liu, W. Wang, H. Chen, Z. Liu, Q. Yu, H. Zeng and L. Sun, *Chemical Communications*, 2013, 49, 10835-10837.
- 35. Q. Fu and J. Liu, *Langmuir*, 2005, **21**, 1162-1165.
- Z. Wang, Y. Wang, Y. Li and B. Liu, *Journal of The Electrochemical Society*, 2010, 157, J125-J129.
- Y. Li, Z. Wang, L. Sun, Z. Wang, S. Wang, X. Liu and Y. Wang, *Materials Research Bulletin*, 2014, 50, 36-41.
- 38. S. Tanabe, K. Tamai, K. Hirao and N. Soga, *Physical Review B*, 1993, 47, 2507.
- S. Gai, G. Yang, X. Li, C. Li, Y. Dai, F. He and P. Yang, *Dalton Transactions*, 2012,
 41, 11716-11724.
- 40. Z. Wang, Y. Wang, Y. Li and H. Zhang, *Journal of Materials Research*, 2011, 26, 693.
- 41. J.-C. Boyer, L. A. Cuccia and J. A. Capobianco, *Nano letters*, 2007, 7, 847-852.
- 42. D. Dexter and J. H. Schulman, *The Journal of Chemical Physics*, 1954, 22, 1063.
- 43. J.-C. Boyer, F. Vetrone, L. A. Cuccia and J. A. Capobianco, *Journal of the American Chemical Society*, 2006, **128**, 7444-7445.
- 44. J. Zhao, Z. Lu, Y. Yin, C. McRae, J. A. Piper, J. M. Dawes, D. Jin and E. M. Goldys,

Nanoscale, 2013, 5, 944-952.

- 45. C. Liu and D. Chen, Journal of Materials Chemistry, 2007, 17, 3875-3880.
- 46. T. Miyakawa and D. Dexter, *Physical Review B*, 1970, 1, 70.
- 47. W. Carnall, P. Fields and K. Rajnak, *The Journal of Chemical Physics*, 1968, 49, 4424.
- 48. J. B. Gruber, M. E. Hills, R. M. Macfarlane, C. A. Morrison, G. A. Turner, G. J. Quarles, G. J. Kintz and L. Esterowitz, *Physical Review B*, 1989, **40**, 9464-9478.
- M. J. Dejneka, A. Streltsov, S. Pal, A. G. Frutos, C. L. Powell, K. Yost, P. K. Yuen, U. Müller and J. Lahiri, *Proceedings of the National Academy of Sciences*, 2003, 100, 389-393.
- Y. Li, Z. Song, C. Li, R. Wan, J. Qiu, Z. Yang, Z. Yin, Y. Yang and Q. Wang, ECS Solid State Letters, 2013, 2, R45-R47.
- 51. C. Hazra, S. Sarkar and V. Mahalingam, *RSC Advances*, 2012, **2**, 6926-6931.
- 52. T. T. Basiev, P. G. Zverev, A. Y. Karasik, S. V. Vassiliev, A. A. Sobol, D. S. Chunaev,
 V. A. Konjushkin, A. I. Zagumennyi, Y. D. Zavartsev, S. A. Kutovoi, V. V. Osiko and I.
 A. Shcherbakov, Stimulated Raman Scattering in YVO4 and GdVO4 Crystals and
 Self RamanFrequency Conversion in Diode Pumped Nd³⁺:GdVO4 Laser, Santa Fe,
 New Mexico, 2004.
- 53. J. Suyver, J. Grimm, M. Van Veen, D. Biner, K. Krämer and H. Güdel, *Journal of Luminescence*, 2006, **117**, 1-12.
- 54. J. Shan, M. Uddi, N. Yao and Y. Ju, Advanced Functional Materials, 2010, 20, 3530-3537.

- 55. M. Kumar, T. K. Seshagiri, R. M. Kadam and S. V. Godbole, *Materials Research Bulletin*, 2011, **46**, 1359-1365.
- 56. L. Guo, Y. Wang, Y. Wang, J. Zhang and P. Dong, *CrystEngComm*, 2012, 14, 3131-3141.