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PAPER

Controllable synthesis and tunable luminescence properties of $Y_2(WO_4)_3$: Ln^{3+} (Ln = Eu, Yb/Er, Yb/Tm and Yb/Ho) 3D hierarchical architectures[†]

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Yttrium tungstate precursors with novel 3D hierarchical architectures assembled from nanosheet building blocks were successfully synthesized by a hydrothermal method with the assistance of sodium dodecyl benzenesulfonate (SDBS). After calcination, the precursors were easily converted to $Y_2(WO_4)_3$ without an obvious change in morphology. The as-prepared precursors and $Y_2(WO_4)_3$ were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) spectra, respectively. The results reveal that the morphology and dimensions of the as-prepared precursors can be effectively tuned by altering the amounts of organic SDBS and the reaction time, and the possible formation mechanism was also proposed. Upon ultraviolet (UV) excitation, the emission of Y₂(WO₄)₃:x mol% Eu³⁺ microcrystals can be tuned from white to red, and the doping concentration of Eu³⁺ has been optimized. Furthermore, the up-conversion (UC) luminescence properties as well as the emission mechanisms of $Y_2(WO_4)_3$: Yb^{3+}/Ln^{3+} (Ln = Er, Tm, Ho) microcrystals were systematically investigated, which show green $(\text{Er}^{3+}, {}^{4}\text{S}_{3/2}, {}^{2}\text{H}_{11/2} \rightarrow {}^{4}\text{I}_{15/2})$, blue $(\text{Tm}^{3+}, {}^{1}\text{G}_{4} \rightarrow {}^{3}\text{H}_{6})$ and yellow (Ho³⁺, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$) luminescence under 980 nm NIR excitation. Moreover, the doping concentration of the Yb³⁺ has been optimized under a fixed concentration of Er³⁺ for the UC emission of $Y_2(WO_4)_3:Yb^{3+}/Er^{3+}$.

1. Introduction

In recent years, the preparation of nano-/micro-materials with novel and controllable morphologies has become an important research issue due to not only the fundamental scientific interest but also for their potential applications in various fields, such as catalysis,¹ optics,² magnetism,³ optoelectronics devices,⁴ solar cells,⁵ and biology.^{6–8} To date, many efforts have been devoted to design and synthesize nano-/micro-materials with diverse morphologies and sizes, such as nanofibers,⁹ nanowires,¹⁰ nanorods,¹¹ nanocubes,¹² microplates,¹³ and hierarchical architectures due to their potential applications in a wide range of fields.¹⁴ Among these morphologies, constructing materials with hierarchical three-dimensional (3D) architectures, self-assembled from basic building blocks (such as 0D nanoparticles, 1D nanorods, and 2D nanoplates or nanosheets) with controllable superstructures have attracted considerable interest for their potential technology applications.^{15–17} As an effective way to control the shape, size, and dimension of the materials, self-assembly driven by various interactions is a fascinating and promising strategy to design 3D ordered hierarchical structures due to the variation of the arrangements of the building blocks.^{18,19} Up to now, a large number of synthetic techniques have been developed to prepare a wide variety of inorganic 3D hierarchical architectures. For example, sandwich-like La₂O₂CO₃ were synthesized through a homogeneous precipitation method,¹⁴ SnO₂ flowers were prepared by a chemical vapor deposition (CVD) method,²⁰ and an electrochemical process was employed for the synthesis of FeOOH star-shaped structures.²¹ Although some progress has been made in the self-assembly synthesis of hierarchical architectures, exploration of rational synthetic routes for controlled construction of complex 3D architectures of other inorganic functional materials via a chemical self-assembly route is still an intensive and hot research topic.²² Furthermore, as a typical solution-based route, a hydrothermal process with great facility and flexibility has been proved to be one of the most effective and convenient approaches in achieving a variety of controllable sizes and morphologies due to its mild reaction conditions, ease of operation, tunable reaction parameters, and abundant organic surfactants.²³⁻²⁶ In particular, various types of surfactants have been widely used in the strategy to achieve morphology and size control, because the functional groups of the organic additives can preferentially adsorb on certain crystal facets and effectively change the surface energies of the crystals, resulting in modulating the kinetics of the crystal growth.²⁷

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As a series of important functional inorganic materials, rare earth (RE) compounds have been extensively studied and employed in various fields, including phosphors,²⁸ polarisers,²⁹ laser host materials,³⁰ catalysis,³¹ solar and other functional materials based on their electronic, optical, and chemical characteristics,³² which originate from electron transitions within the 4f shell and are highly sensitive to the compositions and structures of the rare earth compounds.³³ So far, a wide variety of rare earth compounds, such as metal oxides,²² vanadates,³⁴ phosphates,³² borates,³⁵ molybdates,³⁶ and tungstates, have been extensively reported.¹⁷ Among these compounds, intensive efforts have been concentrated on tungstate materials due to their outstanding properties, which have promising applications in the areas of negative thermal expansion materials³⁷ and quantum electronics and lasers.³⁸ Recently, stimulated by both the promising applications and the interesting properties, much attention has been paid to the photoluminescence properties of $Tb_2(WO_4)_3$ and $Gd_2(WO_4)_3$.^{33,39} However, the preparation and luminescent properties of Y₂(WO₄)₃:Ln with 3D hierarchical structures have received little attention, while intensive efforts have been made in the fabrication of negative thermal expansion materials of $Y_2(WO_4)_3$ using the solid state method.⁴⁰ As an important organic surfactant, sodium dodecyl benzenesulfonate (SDBS) has been extensively employed as a structure-directing agent to kinetically control the growth rates of different crystalline faces by interacting with these faces through adsorption and desorption.^{41–44} To the best of our knowledge, there has been no systematic work about the effect of SDBS on the shape controllable synthesis of $Y_2(WO_4)_3$ with uniform size and morphology, and it has essential meaning to extend the synthetic strategy to controllable fabrication of other inorganic compounds and improve the performance in various fields.

In this paper, we report the morphology controllable synthesis of yttrium tungstate precursors with novel and uniform 3D hierarchical structures *via* a facile and mild hydrothermal route in the presence of SDBS, and the corresponding $Y_2(WO_4)_3$ 3D architectures were obtained by a further heat treatment of the precursors at 800 °C for 2 h. To investigate the formation mechanism of the hierarchical superstructures, a series of time-dependent experiments were carried out. In addition, the down-conversion (DC) PL properties of the as-prepared precursors could be modulated by altering the doping concentration of Eu³⁺, while the UC emission properties of $Y_2(WO_4)_3$:Ln³⁺ (Ln = Yb/Er) could be optimized by tuning the doping concentration of Yb³⁺. Especially, it is the first time to investigate the UC luminescence properties of $Y_2(WO_4)_3$ with a novel 3D hierarchical shape.

2. Experimental section

2.1. Materials

The raw rare-earth oxides, including Ln_2O_3 (Ln = Y, Eu, Yb, Er, Tm, Ho) (99.99%), Na_2WO_4 , sodium dodecyl benzenesulfonate (SDBS), HNO₃ and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals are of analytical grade and used directly without further purification.

2.2. Preparation of drug storage/release system

 $Y(NO_3)_3$ was prepared by dissolving Y_2O_3 in dilute nitric acid, then evaporating the water in the solutions by heating. In a typical process for the synthesis of precursor, 0.5 mmol SDBS was first dissolved in 35 mL deionized water to obtain a transparent solution. Then 1 mmol of Y(NO₃)₃ was added into the above solution to form a white colloidal precipitate. After vigorous stirring for 15 min. 1 mmol Na₂WO₄ was introduced to above reaction system. The pH value of the mixed solution was subsequently adjusted to a value of 5 by adding HNO₃ (1 mol L^{-1}) or NaOH (1 mol L^{-1}). After additional agitation for 30 min, the as-obtained white colloidal precipitate was transferred into a 50 mL autoclave, sealed, and heated at 200 °C for 24 h. As the autoclave was naturally cooled to room temperature, the precipitates were separated by centrifugation, washed with deionized water and ethanol in sequence, and then dried in a vacuum oven 60 °C for 12 h. The final product of $Y_2(WO_4)_3$ was obtained followed by further calcination at 800 °C for 2 h. $Y_2(WO_4)_3:Ln^{3+}$ (Ln = Eu, Yb/Er, Yb/Tm and Yb/Ho) were prepared in a similar procedure except that Eu₂O₃ with Y₂O₃ and Yb2O3/Er2O3, Yb2O3/Tm2O3, Yb2O3/Ho2O3 with Y2O3 were the initial materials, respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 15° \min^{-1} in the 2θ range from 10–50°, with graphite-monochromatized Cu K α radiation ($\lambda = 0.15405$ nm). SEM images were obtained on a scanning electron microscope (JSM-6480A, Japan Electronics) equipped with an energy-dispersive X-ray spectrum (EDS, JEOL JXA-840). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai G² S-Twin instrument with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiple CCD camera. The downconversion (DC) excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorometer equipped with a 150 W xenon lamp as the excitation source. The UC emission spectra were obtained using a 980 nm laser from an OPO (optical parametric oscillator, Continuum Surelite, USA) as the excitation source and detected by a photomultiplier tube (HAHAMATSU R955) from 400-900 nm. Luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a 250 nm laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (ContinuumSunlite OPO). The X-ray photoelectron spectra (XPS) were taken on a VG ESCALAB MK II electron energy spectrometer using Mg K α (1253.6 eV) as the X-ray excitation source. Fourier transform infrared spectroscopy (FT-IR) was carried out in an ABB Bomen FTLA2000-100 spectrometer using KBr pellets. Thermogravimetric analysis and differential scanning calorimetry data were recorded with a thermal analysis instrument (SDT 2960, TA Instruments, New Castle, DE) at the heating rate of 10 °C min⁻¹ in an air flow of 100 mL min⁻¹. All the measurements were performed at room temperature.



Fig. 1 XRD patterns of (A) the yttrium tungstate precursor, (B) the $Y_2(WO_4)_3$ sample after calcination and the standard data for $Y_2(WO_4)_3$ (JCPDS No. 15-0447) as a reference.

3. Results and discussion

3.1. Phase and morphology

Fig. 1 shows the XRD patterns of the as-prepared yttrium tungstate precursor and the corresponding product after calcination treatment, respectively. Compared with all the standard XRD patterns in JCPDS cards, the diffraction peaks of the precursors cannot be indexed to a certain phase because the hydrothermalderived product may contain some hydrous compounds originating from the solution medium,⁴⁵ as shown in Fig. 1A. In Fig. 1B for $Y_2(WO_4)_3$, it can be seen that all the diffraction peaks of the sample can be well indexed to the pure phase of $Y_2(WO_4)_3$ (JCPDS No. 15-0447), indicating that the precursor was completely converted to $Y_2(WO_4)_3$ at 800 °C for 2 h. In addition, it should be pointed out that the XRD pattern presents some differences in the relative intensities according to the standard JCPDS card, suggesting the possibility of different preferential orientation growth of the sample.⁴⁶

To further confirm the surface composition and functional groups of the yttrium tungstate precursor, the sample was subjected to XPS and FT-IR measurements, respectively. Fig. 2 presents the survey XPS spectrum and respective elemental XPS spectra of the as-prepared sample. It can be seen that the binding energies of O (1s, 536 eV), Y (3d, 157 eV), W (4f, 36 eV) and C (1s, 284 eV) can be obviously found, which further confirm the existence of Y, Mo, and O in the sample. In the FT-IR spectrum of the precursor (Fig. S1, ESI⁺), the sharp peaks at 3556 cm^{-1} and the broad band at 3430 cm^{-1} are attributed to the O-H vibration of the coordination water and the surfaceadsorbed water, respectively. The vibration band due to the $-CH_2$ group (2958, 1430 cm⁻¹) may arise from the starting material of SDBS. The peaks at about 962 cm⁻¹ can be attributed to the W=O stretching vibration, while the peaks at 844 and 725 cm⁻¹ are assigned to the W-O stretching vibration. In addition, the thermal behavior of the as-prepared yttrium tungstates precursor was investigated. From the TG curve (Fig. S2, ESI \dagger), it can be found that the total weight loss is about 4.02% between 30 °C and 800 °C, which corresponds to the loss of all non-coordinated and coordinated water molecules. On the basis of the above analysis and the XRD pattern, we can reasonably presume that the final $Y_2(WO_4)_3$ sample may originate from the yttrium tungstate precursor.



Fig. 2 XPS spectra of the yttrium tungstate precursor: (A) wide scan spectrum, (B) W 4f, (C) Y 3d and (D) O 1s.



Fig. 3 (A, B, C) SEM images with different magnifications and (D, E, F) TEM images with different magnifications of yttrium tungstate precursor.

The morphology, dimension and size of the as-synthesized yttrium tungstate precursor were investigated by SEM and TEM. The low-magnification SEM image (Fig. 3A) displays a representative overview of the sample, which indicates that the sample consists of 3D bowknot-like hierarchical microstructures with relatively uniform size distribution. From Fig. 3B, we can see that the as-obtained 3D hierarchical structures have a typical length of about 8 µm with a narrow size distribution. The highmagnification SEM image (Fig. 3C) shows that the bowknot-like microstructure is made up of numerous smooth rectangle 2D anisotropic nanosheet building blocks with a length of about 8 µm and a width of about 2.5 µm. These nanosheets are selfassembled in a separate and cross-linked way to construct the 3D bowknot-like hierarchical architectures, which compactly bond to each other in the middle and split in both sides of the structures. The typical TEM images (Fig. 3D and E) also indicate that numerous nanosheets with very high density radially arrange



Fig. 4 SEM images with different magnification of yttrium tungstate precursors prepared with SDBS amounts of (A, B) 0.5 mmol, (C, D) 0.75 mmol and (E, F) 1.25 mmol at 200 °C for 24 h.

from the center of the bowknot-like structures, which is consistent with the SEM images. In the high-magnification TEM image (Fig. 3F), it can be clearly found that the thickness of the nanosheet building blocks is about 60 nm.

To validate the effect of SDBS on the crystal formation of the products, a series of concentration-dependent experiments were carried out in our current reaction system. Fig. 4 depicts the typical SEM images of the samples prepared at 200 °C for 24 h with different SDBS amount of 0.5, 0.75 and 1.25 mmol, respectively. As shown in Fig. 4A and B, when 0.5 mmol SDBS was introduced, uniform bowknot-like microstructures of about 8 µm in length are obtained, and the width of the splitting both ends is about 2.5 µm. With the increase of the SDBS amount up to 0.75 mmol, the as-prepared sample still keeps the 3D bowknot-like hierarchical shape (Fig. 4C). From the high-magnification SEM image (Fig. 4D), it is obvious that the product obtained with 0.75 mmol SDBS is longer in ends length and has more densely nanosheets building blocks compacted in the middle of the structure, in which the average length and the diameter of the splitting ends is about 8.5 and 6 µm, respectively. When the SDBS amount is increased to 1.25 mmol, the morphology of the product is converted to 3D hierarchical microflowers with an average diameter of 4 µm (Fig. 5E). An individual particle (Fig. 5F) clearly reveals that the single 3D microflowers architecture is composed of a large number of 2D smooth nanoflakes building blocks in a radial way from the center to the surface. On the basis of the above results, we can reasonably infer that the SDBS amount plays an important role in the morphology evolution of the as-prepared yttrium tungstate precursors.



Fig. 5 (A, B, C) SEM images with different magnifications, (D, E) TEM images with different magnifications, (F) EDS spectrum, (G) HRTEM image of $Y_2(WO_4)_3$ sample annealed at 800 °C for 2 h.

Fig. 5 shows typical SEM, TEM, HRTEM images and EDS of Y₂(WO₄)₃ sample obtained at 800 °C for 2 h. In Fig. 5A, it is obvious that the sample is composed of uniform bowknot-like hierarchical microstructures in high yield, which is similar to the precursor. Fig. 5B indicates that the surface of the annealed sample is slightly rough in comparison with that of the precursor due to the gradual elimination of H₂O and CO₂ during the calcination processes. The magnified SEM image (Fig. 5C) shows that Y₂(WO₄)₃ has bowknot-like microstructures, which are selfassembled from 2D anisotropic nanosheet building blocks. Obviously, conversion did not lead to the change in the shape of the final product due to the higher activation energies needed for the collapse of these structures.^{47,48} The TEM image (Fig. 5D) of Y₂(WO₄)₃ indicates that the nanosheets are assembled in a separate and cross-linked form which bond to each other in the middle and split in the side of the structure. Fig. 5E displays the TEM image of a horizontal bowknot-like sample, which also reveals that the bowknot-like structure is self-assembled from many 2D rectangle nanosheets building blocks with a slightly rough surface. In the typical HRTEM image (Fig. 5E), the interplanar spacing (0.695 nm) of the lattice fringes corresponds to the (020) plane of the orthorhombic $Y_2(WO_4)_3$ phase. The EDS spectrum (Fig. 5F) indicates the presence of Y, O, W elements in the final product after annealing, which is consistent with the XRD pattern. Fig. S3 (ESI⁺) presents SEM images of the precursors prepared with 0.75 and 1.25 mmol SDBS and their corresponding SEM images after annealing at 800 °C for 2 h. We can see that the calcined products also inherit the morphologies of their corresponding precursors whereas their surfaces are slightly rougher than those of the precursors.

3.2. Possible growth mechanism

In order to investigate the detailed formation mechanism of the novel bowknot-like hierarchical architectures precursors, we



Fig. 6 SEM images of yttrium tungstate precursors with 0.5 mmol SDBS at 200 °C for a reaction time of (A) 1 h, (B) 3 h, (C) 6 h, (D) 9 h, (E) 12 h, and (F) 24 h.

conducted a series of time-dependent experiments, which are given in Fig. 6. At the initial stage of 1 h, the as-prepared sample is composed of numerous spherical nanoparticles (Fig. 6A). When the reaction time is increased to 3 h, some irregular nanorod-like particles with some aggregation are obtained (Fig. 6B). With further increasing the reaction time to 6 h, a small amount of bundle-like structures formed by many crossed nanosheets and a large number of nanosheets are found (Fig. 6C). Therefore, it is believed that the final perfect bowknotlike microstructure should originate from these nanosheets building blocks. As the reaction time is increased to 9 h (Fig. 6D), we can see that more nanosheets continuously aggregate into the petal of the crossed bundle-like structure, and the 3D bowknotlike hierarchical architectures are gradually developed. At a reaction time of 12 h, both ends of the bowknot-like structure become dense and thick, almost no nanosheet building blocks can be found (Fig. 6E). After the reaction time is further increased to 24 h, the integrated bowknot-like microstructures can be achieved except that the petals are thicker and more compact than those of the sample prepared at 12 h, as shown in Fig. 6F.

On the basis of the above analysis and time-dependent experimental results, we can reasonably infer that the formation of such complicated microstructures is achieved *via* a hierarchical self-assembly process, which is related to the function of the anionic surfactant sodium dodecyl benzenesulfonate (SDBS). As we know, the growth rate of a crystal face is determined by the relative specific energy of each face. The fastest crystal growth will occur in the direction perpendicular to the face with the highest surface energy, resulting in the fast growing planes with high energy disappearing to leave behind the slowest growing planes with low energy.^{49,50} When organic surfactants are introduced during the crystal growth process, the relative order of surface energies can be modified in that the organic molecules of the surfactants can be selectively adsorbed on the surface of the growing nanoparticles, and change the corresponding surface energy of the bound plane, thus the growth rates of different crystallographic directions are varied and lead to a change in the final morphology. As an important organic surfactant, SDBS can tailor the surface energy by capping the surface of nuclei and control the morphology of the crystals. In addition, as previously reported, in the SDBS organic molecules, the functional DBS⁻ group has a strong tendency to coordinate with inorganic metal cations to form complexes through coordination interaction.^{51,52} Under the hydrothermal conditions of high temperature and pressure, inorganic metal cations in the complex will be gradually released when attacked by the free WO_4^{2-} ions in the reaction system, which can control the concentration of free inorganic metal cations in the solution and thus control the nucleation and growth of the crystals in view of the dynamic process.¹⁶ In summary, on the basis of the present experimental results and the previous literature, it is believed that SDBS may have a double function in adjusting the final morphology of the crystal. On the one hand, as a strong chelating ligand, when Y³⁺ ions were added in the solution containing SDBS, the functional group DBS⁻ will form a stable complex with Y³⁺ ions through strong chelating interactions, which will slow down the nucleation and subsequent crystal growth of the $Y_2(WO_4)_3$ precursor, resulting in the formation of 3D microstructures with a narrow size distribution. The Y³⁺–DBS⁻ complexes can be confirmed by the fact that a white precipitate is produced after directly mixing the aqueous solution containing Y^{3+} and DBS⁻. Under the proper hydrothermal conditions, the chelating of Y³⁺–DBS⁻ complexes will be weakened and gradually release Y³⁺ to promote the formation of Y^{3+} -WO₄²⁻ precursor nuclei. On the other hand, as a structure-directing reagent, during the crystal stage, the DBS⁻ molecules with long chains can be selectively adsorbed on a certain active facet. Therefore, the surface energy of the certain facet can be reduced and will become more exposed in areas, while these facets with a higher surface energy will vanish in the final shape. Then many well-defined nanosheets with large scale exposed facets are formed via the subsequent crystallization process, followed by the assembly of these building blocks into 3D hierarchical architectures. With the increase of reaction time, more nanosheets grow on the earlier petals, and make them be more compact and bigger. With increasing the amount of SDBS, more functional groups (DBS⁻) take part in the chelating action of Y³⁺–DBS⁻ complexes, and more nanosheets self-assembly to the petal of the hierarchical microstructure. This should be the reason that the overall morphology changes from sparse to bushy bowknot-like architectures and then to more compact flower-like structures with the increase of the SDBS amounts. The whole process of the morphology evolution of yttrium tungstate precursors is summarized in Scheme 1.

3.3. Luminescent properties

As one kind of important solid-state materials, rare-earth tungstates have been proved to be good host lattices for the



Scheme 1 Schematic illustration for the whole formation process of the yttrium tungstate precursor.



Fig. 7 Excitation and emission spectra of (A) yttrium tungstate precursor doped with 7 mol% Eu^{3+} , and (B) $Y_2(WO_4)_3$:7 mol% Eu^{3+} sample.

luminescence of rare earth ions.^{33,39,53,54} Nevertheless, to the best of our knowledge, the optical properties of $Y_2(WO_4)_3$ doped with rare earth metal ions have rarely been reported. Herein, the bowknot-like samples prepared with 0.5 mmol SDBS were used as representative examples to investigate the luminescence properties of $Y_2(WO_4)_3$:Ln³⁺ (Ln = Eu, Yb/Er, Yb/Tm, Yb/Ho). In addition, to obtain the maximum luminescence intensity of the DC and UC luminescence, the doping concentrations of Eu³⁺ and Yb³⁺ in the hosts have also been optimized. Especially, it is the first time investigating the UC luminescence properties of $Y_2(WO_4)_3$:Ln with 3D hierarchical microstructures.

DC luminescence properties. Fig. 7 presents the PL excitation and emission spectra of the yttrium tungstate precursor and the corresponding $Y_2(WO_4)_3$:7%Eu³⁺ after annealing at 800 °C for 2 h. In Fig. 7A, the excitation spectrum of yttrium tungstate precursor is obtained by monitoring the emission of the Eu³⁺ ⁵D₀ \rightarrow ⁷F₂ transition at 617 nm. It can be seen that the excitation spectrum consists of two main features, a strong and broad band from 200–350 nm with a maximum at 276 nm, which



Fig. 8 (A) Emission spectra and (B) CIE chromaticity diagram of $Y_2(WO_4)_3$ doped with different Eu^{3+} concentrations.

corresponds to the charge transfer absorption from the 2p orbitals of the oxygen ligands to the 5d orbitals of the central tungsten atoms in the WO_4^{2-} groups,¹⁷ and a number of characteristic f–f transition lines within the $Eu^{3+} 4f^6$ configuration in the longer wavelength region between 350 and 450 nm, which are assigned to the transitions from the ${}^{7}F_{0}$ ground state to the Eu³⁺ excited states of ${}^{5}D_{4}$ (363 nm), ${}^{5}G_{2}$ (383 nm), ${}^{5}L_{6}$ (396 nm), and ${}^{5}D_{3}$ (417 nm), respectively. 55 The presence of the excitation peak of the WO_4^{2-} groups in the excitation spectrum of Eu^{3+} indicates that there is an energy transfer from the WO_4^{2-} groups to Eu³⁺ ions in the Eu³⁺ doped yttrium tungstate precursor. Upon excitation into the WO_4^{2-} at 276 nm, the emission spectrum of asprepared precursor is composed of a series of sharp lines centered at 539, 583, 596 and 617 nm, which can be ascribed to the ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0, 1, 2) transitions of the Eu³⁺ ions, ${}^{56-62}$ and the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 617 nm is the most prominent group. Compared with the emission of Eu³⁺, the intrinsic blue emission at about 450 nm from WO_4^{2-} groups is very weak, revealing an efficient energy transfer from WO₄²⁻ groups to Eu³⁺. Fig. 7B shows the excitation and emission spectra of Y₂(WO₄)₃:7%Eu³⁺ obtained at 800 °C for 2 h. As shown, the excitation spectrum monitored by $Eu^{3+} {}^5D_0 \rightarrow {}^7F_2$ at 618 nm comprises a broad band with the maximum at 264 nm and some weak peaks, which are also assigned to the charge transfer transitions within the WO_4^{2-} groups and the characteristic f-f transitions of Eu³⁺ ions, respectively. The emission spectrum of $Y_2(WO_4)_3$:7%Eu³⁺ obtained by excitation into WO_4^{2-} groups at 264 nm contains exclusively the characteristic emissions of Eu³⁺, which are mainly identical to the excitation spectrum of the precursor. In summary, it is clear that there are some difference in the PL spectra of Eu³⁺ doped yttrium tungstate precursor and $Y_2(WO_4)_3$:7%Eu³⁺ sample. First, the broad band in the excitation spectra shifts from 276 nm to 264 nm, which may be due to the conversion from the distorted WO_4^{2-} groups in the precursor to refined ones in $Y_2(WO_4)_3$. Second, the PL intensity of the Y₂(WO₄)₃:7%Eu³⁺ is much stronger and the intensity of the broad WO₄²⁻ groups can hardly be observed compared with those of the precursor, indicating that the energies transfer from WO_4^{2-} groups to Eu³⁺ ions is more efficient in Y₂(WO₄)₃.

Fig. 8A gives the emission spectra of $Y_2(WO_4)_3$: $x \mod W Eu^{3+}$ (x = 1-10) under 264 nm excitation. As shown, with an increase of Eu³⁺ ions concentration up to 7%, the PL intensity of Eu³⁺ ions increases while the intensity of WO₄²⁻ groups decreases due to the enhancement of the energy transfer probability from



Fig. 9 Decay curves for (A) yttrium tungstate precursor doped 7 mol% Eu^{3+} , (B) $Y_2(WO_4)_3$;7 mol% Eu^{3+} sample.



Fig. 10 NIR-to-visible UC emission spectra of (A) $Y_2(WO_4)_3:Yb^{3+}/Er^{3+}$, (B) $Y_2(WO_4)_3:Yb^{3+}/Tm^{3+}$, (C) $Y_2(WO_4)_3:Yb^{3+}/Ho^{3+}$ under 980 nm NIR excitation, and (D) their corresponding CIE chromaticity diagram.

 WO_4^{2-} groups to Eu^{3+} ions and finally almost completely convert to the characteristic emission of Eu^{3+} . When the Eu^{3+} concentration is further increased to 10%, the emission intensity of the Eu^{3+} ions is decreased due to the concentration quenching of the Eu^{3+} ions. Fig. 8B presents the chromaticity diagram for $Y_2(WO_4)_3$:x mol% Eu^{3+} samples with different Eu^{3+} concentration, which reveals that the emission colors can be tuned from blue to white to red only by altering the doping concentration of the Eu^{3+} ions. Notably, the CIE coordinates for the $Y_2(WO_4)_3$:3% Eu^{3+} sample are determined to be x = 0.323, y =0.280, locating in the white light luminescence zone (point B, Fig. 8B), which may be caused by the blue emission of WO_4^{2-} groups and red emission of the doped Eu^{3+} simultaneously.

In the PL decay curves of as-prepared 3D hierarchical yttrium tungstate precursor and the corresponding $Y_2(WO_4)_3$:7%Eu³⁺ (Fig. 9), the ${}^5D_0 \rightarrow {}^7F_2$ transitions of Eu³⁺ ions can be well fitted into a single exponential function as $I = I_0 \exp(-t/\tau)$, where τ is the decay lifetimes and the lifetimes were determined to be 0.368 and 0.497 ms, respectively.

UC luminescence properties. Fig. 10 presents the UC luminescent properties of the $Y_2(WO_4)_3$:3%Yb³⁺/1%Ln³⁺ (Ln = Er, Tm, Ho) microstructures under 980 nm NIR excitation. In



Fig. 11 (A) NIR-to-visible UC emission spectra of $Y_2(WO_4)_3:xYb^{3+}/1\%Er^{3+}$ doped with different Yb^{3+} concentrations (B) their corresponding CIE chromaticity diagram.

Fig. 10A for $Y_2(WO_4)_3$:Yb³⁺/Er³⁺, the three emission bands at around 521 nm, 543 nm and 658 nm can be assigned to the thermalized ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er^{3+} , respectively.^{63–67} The corresponding CIE coordinates for the emission spectrum of $Y_2(WO_4)_3$: Yb³⁺/Er³⁺ are determined as x = 0.178, y = 0.766, locating in the green region (point A, Fig. 10D). As for $Y_2(WO_4)_3$:Yb³⁺/Tm³⁺ (Fig. 10B), the peak centered at 474 nm of blue emission, 643 nm and 693 nm of weaker red emission are ascribed to the transitions of ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$, ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ and ${}^{3}F_{3} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺, respectively.^{68,69} The corresponding CIE coordinates for the emission spectrum of Y₂(WO₄)₃:Yb³⁺/Tm³⁺ are determined as x = 0.152, y = 0.141, which locates in the blue region (point B, Fig. 10D). In the case of $Y_2(WO_4)_3$:Yb³⁺/Ho³⁺ (Fig. 10C), the peak centered at 541 nm can be assigned to the ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transition, and the peak at 660 nm may originate from the ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transition.⁷⁰ The corresponding CIE coordinates for the emission spectrum Y₂(WO₄)₃:Yb³⁺/Ho³⁺ are determined as x = 0.397, y = 0.509, locating in the vellow region (point C, Fig. 10D).

In order to further investigate the UC emission properties of Y₂(WO₄)₃:Yb³⁺/Er³⁺ 3D hierarchical microstructures, a series of experiments with different doping levels of 1%Yb³⁺/1%Er³⁺, 2% $Yb^{3+}/1\%Er^{3+}$, $3\%Yb^{3+}/1\%Er^{3+}$, and $4\%Yb^{3+}/1\%Er^{3+}$ were carried out to seek the optimal doping levels of Yb³⁺/Er³⁺. As shown in Fig. 11A, the emission spectra have no obvious diversification in shape and the major bands differ only in their intensities as a function of Yb³⁺ doping concentration. Obviously, when the doping concentration of Er^{3+} is fixed at 1%, the emission intensity increases with the increased Yb³⁺ concentration from 1% to 3%, and then decreases with further raise of the Yb^{3+} concentration. The results indicates that the $Y_2(WO_4)_3:3\%$ $Yb^{3+}/1\%Er^{3+}$ microstructures have the highest emission intensity under the same measurement conditions. When Yb³⁺ concentration is increased from 1% to 3%, more Yb³⁺ ions become available to furnish and transfer the energy to the Er^{3+} , resulting in the higher emission intensity. As the Yb³⁺ concentration is further increased to a higher concentration of 4%, the Yb³⁺ ions may act as trapping centers and dissipate energy nonradiatively, because the interatomic distance of Yb³⁺ between Er³⁺ decreases with the enhanced amount of Yb³⁺, which remarkably enhances the probability of energy migration to the quenching center caused by resonance transfer, resulting in the concentrationdependent quenching.⁷¹ The respective CIE coordinates for the



Fig. 12 The proposed energy transfer mechanisms under 980 nm NIR excitation in $Y_2(WO_4)_3$:Yb³⁺/Er³⁺, $Y_2(WO_4)_3$:Yb³⁺/Tm³⁺ and $Y_2(WO_4)_3$:Yb³⁺/Ho³⁺.

UC emission spectra of $Y_2(WO_4)_3$:Yb³⁺/Er³⁺ with different Yb³⁺ doping concentrations are given in Fig. 11B. The difference of the CIE chromaticity values is due to the different green to red intensity ratios for the samples.

The proposed UC mechanism in $Y_2(WO_4)_3$: Yb^{3+}/Ln^{3+} (Ln = Er, Tm, Ho) is described in the energy diagram, as shown in Fig. 12. When excited at 980 nm, the Yb³⁺ in the ${}^{4}F_{7/2}$ ground state can absorb the photon and promote to its excited ${}^{2}F_{5/2}$ state. For $Y_2(WO_4)_3$:Yb³⁺/Er³⁺ (Fig. 12, left), the ${}^{3+}$ ion from ${}^{4}F_{7/2}$ to ${}^{4}F_{5/2}$ process promotes a Er³⁺ ion from ground state ${}^{4}I_{15/2}$ to ${}^{4}I_{11/2}$ by transferring the energy to a Er^{3+} ion, and then the excited Er^{3+} ion transits to a higher ${}^{4}\mathrm{F}_{7/2}$ level when another Yb^{3+} ion at excited-state ${}^{4}F_{5/2}$ continuously transfers the energy to the Er³⁺ ion. The populated ${}^{4}F_{7/2}$ level decays non-radiatively to the lowlying ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ states of Er^{3+} ions, and produces emissions at 521 and 543 nm with a radiative transition to ground state ${}^{4}I_{15/2}$, respectively. Alternatively, some of the excited Er³⁺ ion electrons can further relax and populate the ${}^{4}F_{9/2}$ level, which results in a red ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emission at 658 nm. For Y₂(WO₄)₃:Yb³⁺/Tm³⁺ (Fig. 12, middle), the first photon of infrared irradiation elevates an electron to ${}^{2}F_{5/2}$ and transfer the energy to Tm $^{3+}$, then it can promote an electron from ${}^{3}H_{6}$ to and ${}^{3}H_{5}$, and Tm³⁺ ion at ${}^{3}H_{5}$ relaxes non-radiatively to 3F_4 . The Tm $^{3+}$ ions in the 3F_4 excited states also can absorb the energy from another Yb³⁺ ion, leading to the Tm^{3+} ion at ${}^{3}F_{4}$ transits to ${}^{3}F_{2}$, then decays to ${}^{3}F_{3}$ and decays non-radiatively from the ³F₃ to ³H₆ with a red emission at 693 nm. At the same time, some Tm^{3+} ions decay from ${}^{3}F_{2}$ to ${}^{3}\text{H}_{4}$ states, which can be excited by a subsequent Yb³⁺ ion, the Tm^{3+} ion at ${}^{3}H_{4}$ is excited to ${}^{1}G_{4}$, and then finally decays nonradiatively to the ${}^{3}H_{6}$ and ${}^{3}F_{4}$, producing blue emission at a weak red emission at 474 and 649 nm, respectively. Similarly, in the case of Y₂(WO₄)₃:Yb³⁺/Ho³⁺ (Fig. 12, right), the energy levels of Ho³⁺ ion are also excited by an initial energy transfer from the excited-state Yb³⁺ ions, then a few subsequent energy transfer processes from Yb^{3+} ions populate the upper Ho^{3+} levels, resulting in the various colors of green emission at 541 nm and a weak red emission at 660 nm, which are ascribed to the ${}^5S_2 \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$ transitions of $Ho^{3+},$ respectively.

4. Conclusion

In summary, we systematically studied the morphology, size and dimension evolution of yttrium tungstate precursors through a hydrothermal method using SDBS as the chelating surfactant.

By simply changing the SDBS amounts, we can tune the morphology and dimension of yttrium tungstate precursors from 3D hierarchical bowknot-like microstructure to flower-like microstructures. The Y₂(WO₄)₃ sample can be obtained from the precursor by a simple annealing process without changing their original morphologies. The crystal growth mechanism was proposed for the formation of this hierarchical structure. Under UV excitation, the as-annealed Y2(WO4)3:Eu3+ hierarchical microstructures emit white to red emissions by simply altering the doping Eu³⁺ concentration. Upon 980 nm NIR laser excitation, Yb^{3+}/Er^{3+} , Yb^{3+}/Tm^{3+} and Yb^{3+}/Ho^{3+} doped $Y_2(WO_4)_3$ exhibit strong green, blue and yellow UC luminescence. Moreover, on the basis of the green up-conversion emission performance, the Yb³⁺ concentration doped in the Y₂(WO₄)₃:Yb³⁺/Er³⁺ samples has been optimized. The 3D hierarchical microstructures with a novel morphology and tunable PL properties might have potential applications in various fields. We believe that the synthetic strategy demonstrated here can also be extended to the controllable synthesis of other inorganic compounds by adjusting the amount of surfactant.

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