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Supplementary Information

For

NaYF₄:Yb³⁺,Tm³⁺Inverse Opal Photonic Crystals and NaYF₄:Yb³⁺,Tm³⁺/TiO2 composites: Synthesis, Highly Improved Upconversion Properties and NIR

Photoelectric Response

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1. Experimental section

All chemicals were of analytical grade and were used as received without further purification. All the lanthanide nitrates were purchased from the National Engineering Research Centre of Rare Earth Metallurgy and Function Materials. Sodium citrate, methyl methacrylate (MMA), ethanol, and citric acid were received from Beijing Chemical Plant (Beijing, P. R. China).

1.1 Preparation of PMMA latex spheres

The PMMA latex spheres were synthesized following the steps below. First, methyl methacrylate (MMA) was washed with NaOH solution (0.01 g/ml) to remove the polymerization inhibitor. Second, 3 ml MMA solution and 40 ml deionized water were put into a three-necked bottle. Polymerization was performed by oil bath heating at 90 °C for 1.5 h with magnetic stirring and 18 mg of potassium persulfate as an initiator. Finally, the milk white solution with suspended PMMA spheres was

obtained. By changing the amount of MMA solution in the above recipe, the diameter of PMMA spheres could be perfectly tuned.

1.2 Preparation of PMMA opal templates

PMMA opal templates were synthesized through the vertical deposition method by growing the PMMA latex spheres onto the glass substrate. First, 60 ml deionized water and 3 ml of the precursor solution were prepared before being put into a 100 ml plastic beaker. Second, a hydrophilic glass substrate was vertically inserted into the plastic beaker. The solution was naturally evaporated in a drying oven at 32 °C for 24 h, and the PMMA latex spheres self-assembled on the glass substrate through hydrophilic interactions. Finally, the opal templates were put into the drying oven at 120 °C for 40 min to improve their physical stability. Additionally, the PBG of the opal templates can be finely controlled via the diameter of the PMMA latex spheres.

1.3 Preparation of Y₂O₃ IOPC templates

 Y_2O_3 IOPC templates were fabricated by the sol-gel method combined with a PMMA opal template technique. In the preparation of the Y_2O_3 precursor solutions, appropriate amounts of $Y(NO_3)_3 \cdot 6H_2O$ and citric acid were dissolved in ethanol. Citric acid was used as the chelating agent and the mixture was stirred for 1 h to form a homogeneous solution. The prepared precursor solutions were used to infiltrate into the voids of the opal template through capillary force. The resulting products were dried in air at room temperature for 24 h and heated to 500 °C at a heating rate of 1 °C·min⁻¹, kept at 500 °C in air for 3 h, then slowly cool to room temperature.

1.4 Preparation of NaYF₄ IOPCs

NaYF₄ IOPCs were prepared through Y_2O_3 IOPC template based solvent-thermal method. First, appropriate amounts of sodium fluoride and sodium citrate were dissolved in deionized water, add ethanol in accordance with the volume ratio of 1:1 and adjust the pH value to 10 via ammonia. Second, put the Y_2O_3 IOPC template into reaction kettle and react with sodium fluoride at 180 °C for 2 h. Finally, rinse the samples with ethanol and dry it in oven at 50 °C for 10 min. Figure 1(a) shows the whole synthetic flow chart for NaYF₄ IOPCs.

1.5 Measurements

The morphology of the samples was measured with a JEOL JSM-7500 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 15 kV. X-ray

diffraction (XRD) patterns of the samples were obtained using a Rigaku D/Max-Ra Xray diffractometer with a monochromatized Cu target radiation resource (λ =1.54Å). Ultraviolet-visible (UVvis) absorption spectra were measured using a Shimadzu UV-3101PC scanning spectrophotometer. The Fourier transform infrared (FTIR) absorption spectra were measured using a Shimadzu DT-40 model 883 IR spectrophotometer. In the measurements of the UCL and infrared emission spectra, a continuous 980 nm wavelength was used to pump the samples. A visible photomultiplier (300–850 nm) and an infrared InAsGa detector (800–2200 nm) combined with a double-grating monochromator were used for spectral collection in the range of 400–2200 nm. The UC luminescent dynamics were investigated using a laser system consisting of a (i) Nd:YAG pumping laser (1064 nm), (ii) third-order harmonic generator (355 nm), and (iii) tunable optical parametric oscillator (OPO, Continuum Precision II 8000) with a pulse duration of 10 ns, repetition frequency of 10 Hz, and line width of 4–7 cm⁻¹. Its output wavelength was fixed at 980 nm.

2. The influence of reaction time



Fig. S1 The SEM images of NaYF₄ inverse opal PhCs at different reaction times, 1 h (a), 2 h (b), 3 h (c), 4 h (d). And the corresponding particle size distribution diagrams, 1 h (e), 2 h (f), 3 h (g), 4 h

(h). The transmittance spectra (i) and the X-ray diffraction (XRD) patterns (j) of the Y_2O_3 inverse opal template and the NaYF₄ inverse opal PhCs at different reaction times. Scale bar: 200 nm.

In solvent-thermal process, the reaction time is an important parameter which directly affects the properties of NaYF₄ IOPCs. Fig S1(a)-(d) show the SEM images of NaYF₄ IOPCs with different reaction times (1 h, 2 h, 3 h and 4 h), respectively. The other conditions were controlled the same (with a pH value of 10 and at 180 °C). It is obvious that the IOPC structures could perfectly remain within 3 h but seriously destroy after 4 h. Furthermore, the particle size of NaYF₄ grows larger as the increasing of reaction time. Fig. S1(e)-(h) display the particle size distribution and the size of the NaYF₄ particles gradually increases from 31 to 84 nm. Figure 1(i) shows the transmission spectra of Y_2O_3 IOPC template and NaYF₄ IOPCs with different reaction times (1 h, 2 h and 3 h). The PBG of PMMA opal template locates at 810 nm, but which of Y₂O₃ IOPC template is 555 nm. Due to a lower average refractive index caused by air spheres instead of polymer spheres and shrinkage of the spheres' diameter during calcination, the PBG of the Y₂O₃ IOPC template has an evident blue shift. As shown in Fig. S1(i), the PBG of NaYF₄ IOPCs gradually shifts to the long wavelength side with the increasing of reacting time. Theoretically, the normal positions of the PBG in FCC IOPCs can be estimated by Bragg's law of diffraction combined with Snell's law as follows,

$$\lambda = \frac{2d_{hkl}}{m} \sqrt{n_{eff}^2 - \sin^2\theta} = 1.633Dn_{eff}$$
(1)

$$n_{eff} = xn_{NaYF_4} + (1-x)n_{air}$$
⁽²⁾

where, λ is the central wavelength of the PBG, *m* is the order of the Bragg diffraction, d_{hkl} is the *hkl* plane distance, n_{eff} is the average refractive index, n_{NaYF4} is the refractive index of NaYF₄, n_{air} is the refractive index of air, *x* is the filling factor, ϑ is the angle from the incident light to the normal of the substrate surface, and *D* is the center-to-center distance of the neighboring hollow spheres. As shown in Fig. S1(a)-(d), the center-to-center distance rarely changes during the increasing of reaction time, but the filling factor becomes larger duo to the change of the particle size of NaYF₄. Deducing from the equations above, the central wavelength of the PBG will be redshift. The PBG of NaYF₄ IOPCs can be continuous adjusted through the accurate control of the reaction time and the diameters of PMMA latex spheres. Fig. S1(j) shows the XRD patterns of the Y₂O₃ IOPC template and the NaYF₄ IOPCs with different reaction times. According to JCPDS standard cards, the Y₂O₃ IOPC template can be indexed successfully to the cubic crystal system (JCPDS 86-1326), as well as the NaYF₄ IOPCs with reaction times of 1 h, 2 h and 3 h (JCPDS 77-2042). However, when the reaction time increases to 4 h, there are both cubic phase and hexagonal phase in the NaYF₄ IOPC sample. Thus it can be seen that the phase of NaYF₄ IOPCs is closely related to the reaction times; and in order to get pure phase, the reaction time must be controlled within 3 h.

3 The lifetime of Tm³⁺ in NaYF₄ IOPCs with different PBGs

The PBGs of NaYF₄ IOPCs were controlled to be 405 nm (PhC1) and 472 nm (PhC2) and the emission line come from the ${}^{1}G_{4}-{}^{3}H_{6}$ is right corresponding to the PBG of PhC2. The luminescence dynamic processes of ${}^{1}D_{2}-{}^{3}H_{6}$, and ${}^{1}G_{4}-{}^{3}H_{6}$, were investigated and shown in Fig. S2. Because trivalent RE ions with 4f–4f inner-shell transitions possess a narrow emission line, the transition of which could be simplified into a two-level system. When the density of states (DOS) in weakly coupled PhCs is modified in a certain direction, the angular-averaged DOS varied little from that of free space.



Fig. S2 The lifetime constant of ${}^{1}D_{2}$ - ${}^{3}H_{6}$ and ${}^{1}G_{4}$ - ${}^{3}H_{6}$ of Tm $^{3+}$ in NaYF₄ IOPCs with PBGs at 405 nm and 472 nm.

4 the Inhibition of local temperature

The luminescence intensity ratio of ${}^{2}H_{11/2}{}^{-4}I_{15/2}$ to ${}^{4}S_{3/2}{}^{-4}I_{15/2}$ of Er³⁺ is very sensitive to temperature, which turns bigger as the increasing of temperature. In order to compare the local temperature of IOPC sample and powder sample under the excitation of the 980 nm light with the same power density, the steady-state spectra of NaYF₄: 20%Yb³⁺, 2%Er³⁺ IOPC sample and powder sample were measured under 0.63W/mm². As shown in Fig. S3, The luminescence intensity ratio of ${}^{2}H_{11/2}{}^{-4}I_{15/2}$ to ${}^{4}S_{3/2}{}^{-4}I_{15/2}$ in IOPC sample is smaller than powder sample, indicating that the IOPC structure can suppress the local thermal effect induced by laser irradiation, which is attributed to its better thermal diffusion property due to the empty cavity structure.



Fig. S3 The steady-state spectra of NaYF₄: 20%Yb³⁺, 2%Er³⁺ IOPC sample and powder sample were measured under 0.63W/mm².