Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Electronic Supplementary Material (ESI) for ChemComm.

Facile synthesis of sub-10 nm-sized bright red-emitting upconversion nanophosphors via tetrahedral YOF:Yb,Er seed-mediated growth

Misun Kang,[a] Han Byul Kang,[a] Sangmoon Park[b] and Ho Seong Jang*[a,c]

[a]Materials Architecturing Research Center, Korea Institute of Science and Technology, 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea

[b]Department of Engineering in Energy & Applied Chemistry, Silla University, Busan 617-736, Republic of Korea

[c]Division of Nano & Information Technology, KIST School, Korea University of Science and Technology (UST), Seoul 02792, Republic of Korea

*Address correspondence to: msekorea@kist.re.kr

Experimental Section

Materials. $YCl_3 \cdot 6H_2O$ (99.99%), $GdCl_3 \cdot 6H_2O$ (99%), $YbCl_3 \cdot 6H_2O$ (99.9%), $ErCl_3 \cdot 6H_2O$ (99.9%), NH_4F (≥99.99%), NaOH (99.99%), oleylamine (OM, technical grade 70%), oleic acid (OA, technical grade 90%), and 1-octadecene (ODE, technical grade 90%) were purchased from Sigma-Aldrich. Sodium oleate (≥97.0%) was obtained from TCI.

Synthesis of YOF:Yb(18%),Er(2%) core upconversion nanophosphors (UCNs). One mmol of $RE(oleate)_3$ [RE: rare earth = 80% Y, 18% Yb, and 2% Er] was prepared by adapting the previous method.[S1] Then, 1 mmol of $RE(oleate)_3$ was mixed with OM and ODE in a three-neck flask (OM:ODE = 6 mL:14 mL, 8 mL:12 mL, 10 mL:10 mL, 12 mL:8 mL, and 14 mL:6 mL), and the temperature of the mixed solution was increased to 150 °C and maintained for 40 min. The homogeneous solution was cooled to 50 °C and methanol (MeOH) solution, which contained 1 mmol of NH_4F, was added to the flask. After keeping the mixed solution at 50 °C for 40 min, MeOH was removed and the solution was heated to various temperatures from 280 °C to 310 °C. After heat-treatment, the as-synthesized YOF:Yb(18%),Er(2%) (YOF:Yb,Er) UCNs were washed with ethanol (EtOH) several times, and they were dispersed in 10 mL of $CHCl_3$.

Syntheses of Gd(20%)-substituted YOF:Yb(18%),Er(2%) and GdOF:Yb(18%),Er(2%) UCNs. One mmol of $RE(oleate)_3$ [RE = 20% Gd, 60%Y, 18% Yb, and 2% Er for Gd(20%)-substituted YOF:Yb(18%),Er(2%), and 80% Gd, 18% Yb, and 2% Er for GdOF:Yb(18%),Er(2%)] was prepared by adapting the previous method.[S1]

Then, 1 mmol of RE(oleate)$_3$ was mixed with OM (10 mL) and ODE (10 mL) in a three-neck flask, and the temperature of the mixed solution was increased to 150 °C and maintained for 40 min. Other synthetic procedure was the same as that for the synthesis of the YOF:Yb,Er UCNs. It is noted that final heat-treatment was conducted at 300 °C. The as-synthesized Gd(20%)-substituted YOF:Yb(18%),Er(2%) and GdOF:Yb(18%),Er(2%) UCNs were dispersed in 10 mL $CHCl_3$, respectively.

Synthesis of YOF:Yb(18%),Er(2%)/YOF core/shell (C/S) UCNs. One mmol of Y(oleate)$_3$ was loaded in a three-neck flask containing OM (10 mL) and ODE (10 mL) solvents and the mixture was heat-treated at 150 °C for 40 min. After cooling down to 50 °C, the YOF:Yb,Er cores and 10 mL of MeOH solution containing 1 mmol of NH_4F were sequentially injected into the solution, and then the reaction solution was kept for 40 min. After removing MeOH, the solution was heat-treated at 300 °C for 90 min. After finishing the heat-treatment, the as-synthesized YOF:Yb(18%),Er(2%)/YOF (YOF:Yb,Er/YOF) C/S UCNs were washed with EtOH several times, and dispersed in 10 mL of $CHCl_3$.

Synthesis of $NaGdF_4$:Yb(18%),Er(2%) core UCNs. The green-emitting UCNs were synthesized by adopting the previously reported method with slight modifacation.[S2] One mmol of $RECl_3 \cdot 6H_2O$ [RE = 80% Gd, 18% Yb, and 2% Er] was mixed with OA (6 mL) and ODE (15 mL) in a three-neck flask, and the temperature of the mixed solution was increased to 150 °C and maintained for 40 min. The homogeneous solution was cooled to 50 °C and MeOH solution, which contained 2.5 mmol of NaOH and 4 mmol of NH_4F, was added to the flask. After keeping the mixed solution at 50 °C for 40 min, MeOH was removed and the solution was heated to 300 °C. After heat-treatment for 60 min, the as-synthesized $NaGdF_4$:Yb(18%),Er(2%) ($NaGdF_4$:Yb,Er) UCNs were washed with EtOH several times, and they were dispersed in 10 mL of $CHCl_3$.

Synthesis of $NaGdF_4$:Yb(18%),Er(2%)/$NaGdF_4$ C/S UCNs. One mmol of $GdCl_3 \cdot 6H_2O$ was loaded in a three-neck flask containing OA (6 mL) and ODE (15 mL) solvents and the mixture was heat-treated at 150 °C for 40 min. After cooling down to 50 °C, the $NaGdF_4$:Yb,Er cores and 10 mL of MeOH solution containing 2.5 mmol of NaOH and 4 mmol of NH_4F were sequentially injected into the solution, and then the reaction solution was kept for 40 min. After removing MeOH, the solution was heated to 300 °C. After the heat-treatment for 60 min, the as-synthesized $NaGdF_4$:Yb(18%),Er(2%)/$NaGdF_4$ ($NaGdF_4$:Yb,Er/$NaGdF_4$) C/S UCNs were washed with EtOH several times, and dispersed in 10 mL of $CHCl_3$.

Characterization. A Hitachi F-7000 spectrophotometer was employed for all photoluminescence (PL) measurements by coupling with a continuous-wave (cw) near infrared (NIR) laser (λ = 980 nm). For

transmission electron microscopy (TEM), an FEI Tecnai G^2 F20 transmission electron microscope was used (operation voltage = 200 kV). The scanning transmission electron microscopy (STEM) images were obtained using an FEI Titan 80/300 scanning transmission electron microscope (operating voltage = 300 kV). The crystal structures of the core and C/S UCNs were determined by using a Bruker D8-Advance X-ray diffractometer operated at 45 kV and 40 mA.

References

S1. H. S. Jang, K. Woo and K. Lim, *Opt. Express*, 2012, **20**, 17107- 17118.

S2. J. E. Choi, D. Kim and H. S. Jang, *Chem. Commun*., 2019, **55**, 2261-2264.

S3. D. Chen, L. Liu, P. Huang, M. Ding, J. Zhong and Z. Ji, *J. Phys. Chem. Lett.*, 2015, **6**, 2833-2840.

S4. J. Wang, F. Wang, C. Wang, Z. Liu and X. Liu, *Angew. Chem. Int. Ed.*, 2011, **50**, 10369-10372.

S5. Q. Chen, X. Xie, B. Huang, L. Liang, S. Han, Z. Yi, Y. Wang, Y. Li, D. Fan, L. Huang and X. Liu, *Angew. Chem. Int. Ed.*, 2017, **56**, 7605-7609.

S6. N. J. J. Johnson, S. He, S. Diao, E. M. Chan, H. Dai and A. Almutairi, *J. Am. Chem. Soc.*, 2017, **139**, 3275-3282.

S7. A.-R. Hong, Y. Kim, T. S. Lee, S. Kim, K. Lee, G. Kim and H. S. Jang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 12331-12340.

S8. G. Yi, Y. Peng and Z. Gao, *Chem. Mater.*, 2011, **23**, 2729-2734.

S9. G. Tian, Z. Gu, L. Zhou, W. Yin, X. Liu, L. Yan, S. Jin, W. Ren, G. Xing, S. Li and Y. Zhao, *Adv. Mater*. 2012, **24**, 1226-1231.

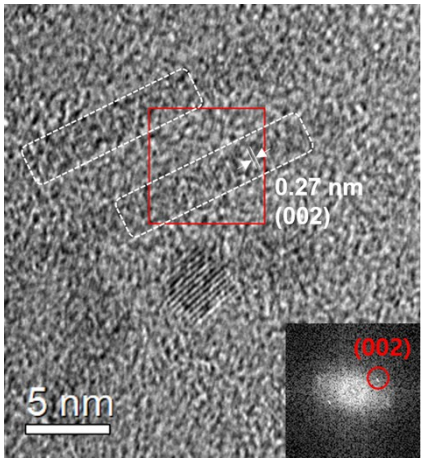

Figure S1. An HR-TEM image of YOF:Yb(18%),Er(2%) UCNs synthesized under the mixed solvent of OM and ODE (OM:ODE = 6:14). Inset shows an FFT pattern obatined for the selected area indicated with a red square.

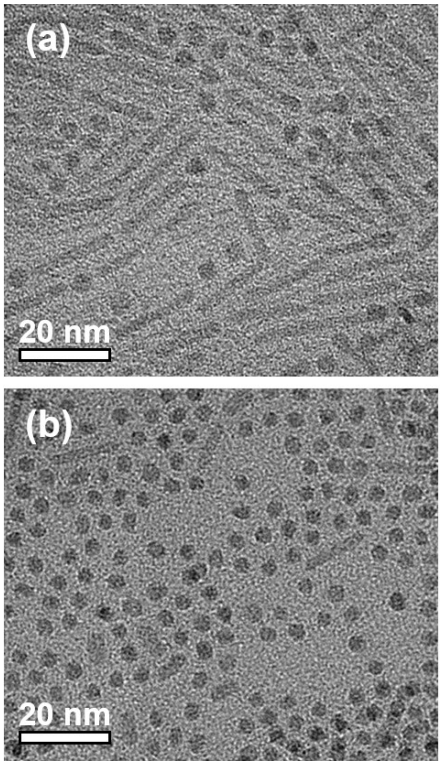

Figure S2. TEM images of (a) Gd(20%)-substituted YOF:Yb(18%),Er(2%) UCNs and (b) GdOF:Yb(18%),Er(2%) UCNs.

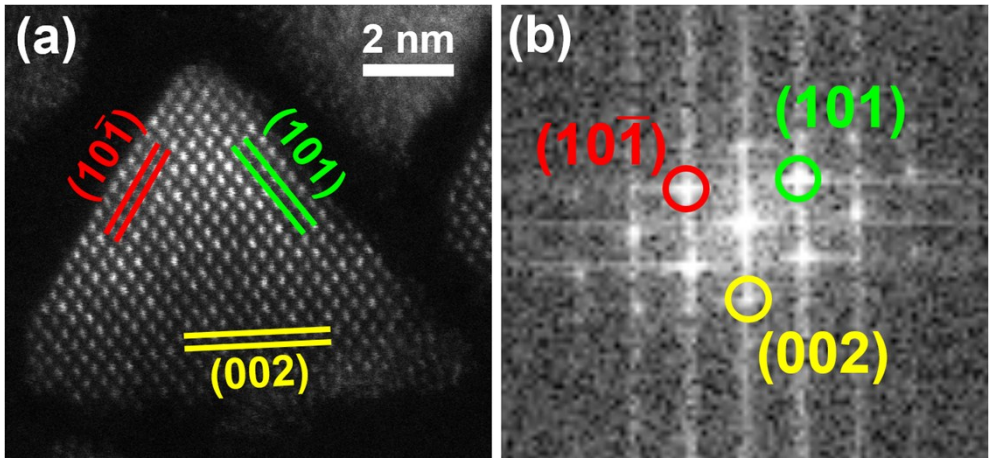

Figure S3. (a) An HR-STEM image of an YOF:Yb(18%),Er(2%) core UCN and (b) an FFT pattern for the HR-STEM image shown in (a).

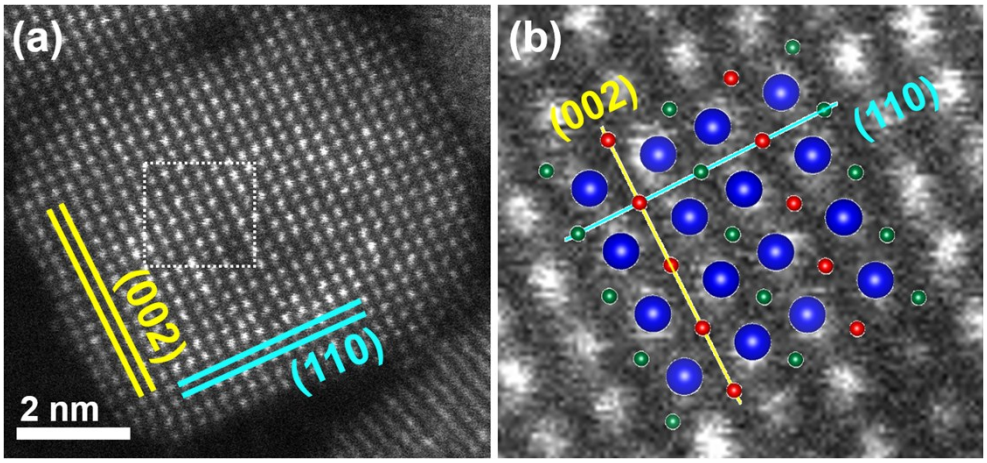

Figure S4. (a) An HR-STEM image of the YOF:Yb(18%),Er(2%)/YOF C/S UCN and (b) an enlarged HR-STEM image of the selected area shown in (a) which is indicated with the white dotted square. Blue, green, and red spheres in (b) represent Y, F, and O, respectively. The atomic arrangement shown in (b) is consistent with a projection of the extended YOF unit cell along the $[1\bar{1}0]$ direction.

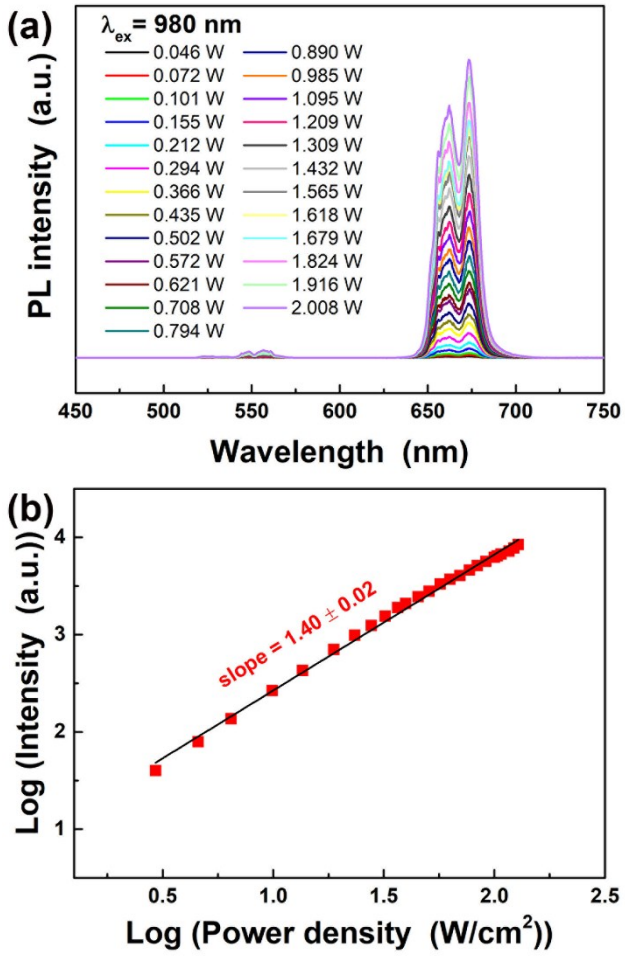

Figure S5. (a) PL spectra of YOF:Yb(18%),Er(2%)/YOF C/S UCNs with varying incident laser powers and (b) The PL intensities for red emission of YOF:Yb(18%),Er(2%)/YOF C/S UCNs as a function of incident laser power density. It is noted that R^2 value for the linear fitting was 0.995.

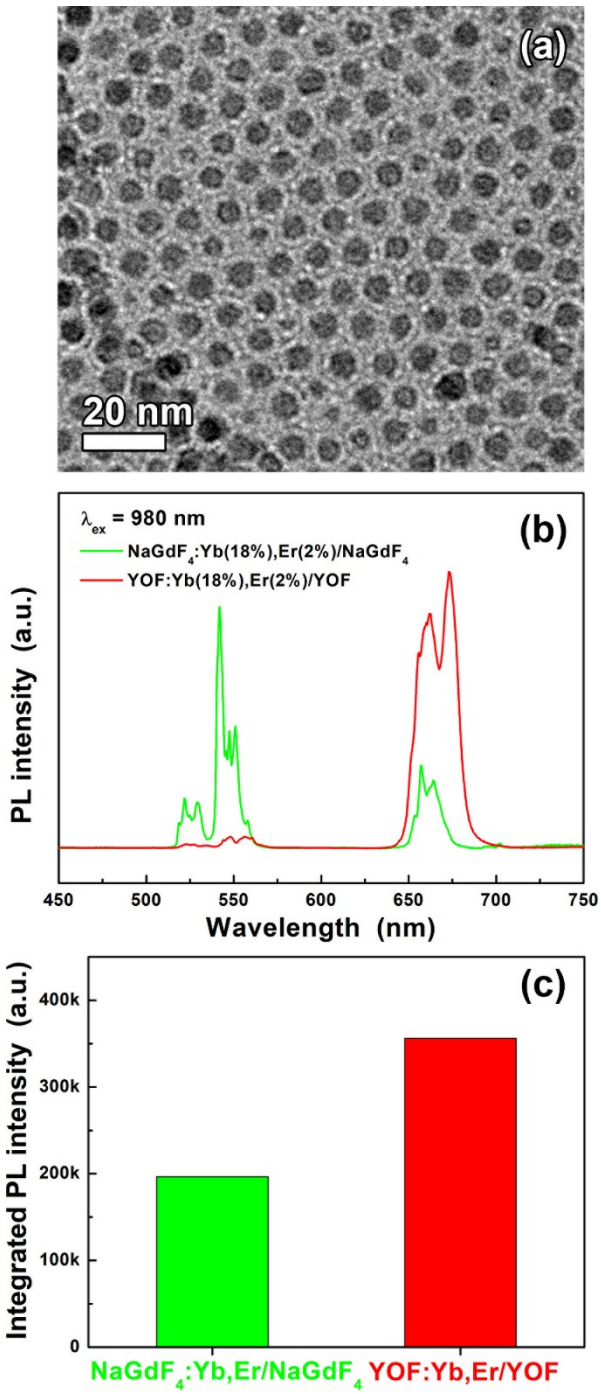

Figure S6. (a) TEM image of $NaGdF_4$:Yb(18%),Er(2%)/$NaGdF_4$ C/S UCNs. (b) PL spectra and (c) integrated PL intensities of the $NaGdF_4$:Yb(18%),Er(2%)/$NaGdF_4$ C/S UCNs and YOF:Yb(18%),Er(2%)/YOF C/S UCNs.

Table S1. Sizes and compositions of some representative red-emitting UCNs.

Composition	size	Reference
YOF:Yb(18%),Er(2%)/YOF	8.7 ± 0.7 nm	This work
$NaGdF_4$:Yb(20%),Ho(1%),Ce(30%)/$NaYF_4$:Nd(20%), Yb(20%)	~50 nm × ~22 nm (diameter × thickness)	S3
$KMnF_3$:Yb(18%),Er(2%)	~15 nm – ~39.6 nm*	S4
$NaErF_4$:Tm(0.5%)/$NaYF_4$	28.6 nm	S5
$NaErF_4$/$NaLuF_4$	~35 – 38 nm / 23.9 ± 1.0 – 33.8 ± 1.1 nm	S6
$NaErF_4$:Tm(0.5%),Gd(10%)/$NaYF_4$:Ca(20%),Yb(10%)/ $NaYF_4$:Nd(40%),Yb(10%)	23.1 nm	S2
$NaGdF_4$:Yb(18%),Ho(2%),Ce(30%)/$NaYF_4$:Nd(50%), Yb(5%)/$NaGdF_4$	19.5 nm	S7
YOF:Yb(20%),Er(2%)/YOF	18 ± 0.7 nm	S8
Mn(30%)-doped $NaYF_4$:Yb(18%),Er(2%)	20 – 25 nm	S9

*Particle size was calculated by using the TEM image in ref. S4.