Supporting Information

Phase Segregation Enabled Scandium Fluoride–Lanthanide Fluoride Janus Nanoparticles

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Experimental Section

Chemicals. RE oxides were purchased from China Rare Earth Online Co., Ltd. Lithium trifluoroacetate (Li(TFA), 97%) was purchased from Alfa Aesar. Oleic acid (OA, >90%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. Oleylamine (OM, >80%) and ammonium trifluoroacetate (NH₄(TFA), 98%) were purchased from Acros. 1-octodecene (ODE, >90%) was purchased from J&K. Ethanol (AR) and cyclohexane (AR) were purchased from Beijing Chemical Works. All the reagents were used as received without further purification.

Precursor preparation. RE(CF₃COO)₃ (RE(TFA)₃) was prepared according to the following steps. 10 g RE oxides and 20–30 mL deionized water were added into a one-necked flask. Excess amount of trifluoroacetate acid (n_{TFA} : $n_{RE} = 4$:1) was then added into the mixture dropwise. The solution was kept at 80 °C with a reflux condenser until the solution became clear. The clear solution was transferred into an evaporation pan and concentrated and dried to obtain solid RE(CF₃COO)₃ powder.

Synthesis of ScF₃–LiYbF₄ Janus NPs in one pot. 1.5 mmol Li(TFA) and 1 mmol RE(TFA)₃ (RE = Sc and Yb; Sc:Yb = 0.78:0.22) were loaded into a mixture of OA (10 mmol), OM (10 mmol) and ODE (20 mmol) in a 100 mL three-necked flask at room temperature. The slurry was heated to 110 \degree for 15 min to remove oxygen and water with vigorous stirring. After that, a clear solution formed and was then heated to 320 \degree . The reaction was maintained at this temperature for 1 h under N₂ atmosphere. Upon cooling to room temperature, an excess amount of ethanol was added to precipitate the NPs. The products were collected by centrifugation at 7800 rpm for 10 min and then washed with ethanol for several times. Finally, the NPs were redispersed in 10 mL cyclohexane for characterizations.

Synthesis of ScF₃–LiLnF₄, ScF₃–LnF₃, and Er³⁺/Ho³⁺/Tm³⁺ doped ScF₃–LiYbF₄ Janus NPs in one pot. The synthetic procedures are similar to that of ScF₃–LiYbF₄ Janus NPs except that the same amount of corresponding Ln(TFA)₃ or a certain concentration of Er/Ho/Tm(TFA)₃ is added into the reaction system to replace Yb(TFA)₃.

Synthesis of NPs by seed-growth method. The seed-growth synthesis method refers to anisotropic nucleation of guest materials on the host crystals, thus feeding precursors of host crystal precedes feeding guest material precursors. Here define that feeding host crystal precursors (Sc(TFA)₃) precedes feeding guest material precursors (Li(TFA) and Yb(TFA)₃) as ScF₃ and Li⁺/Yb³⁺, and the preparation of final products (ScF₃ and Li⁺/Yb³⁺) is taken as an example:

Solvent mixture A of OA (7.5 mmol) and OM (7.5 mmol) was loaded into a 100 mL three-necked flask A at room temperature. The mixture was then heated to 110 °C for 15 min and subsequently heated to 320 °C under N₂ atmosphere. At the same time, mixture B containing 0.78 mmol Sc(TFA)₃, 2.5 mmol OA, 2.5 mmol OM and 20 mmol ODE was injected into mixture A at a speed of 10 mL/h. After 1 h, 0.1 mL reaction mixture was extracted for further characterizations. Meanwhile, a solvent mixture C (OA/OM/ODE = 5/5/10 mmol) containing 1.5 mmol Li(TFA) and 0.22 mmol Yb(TFA)₃ was injected into the reaction mixture, which was kept at 320 °C for 30 min.

Here define that feeding host crystal precursors (Sc(TFA)₃ and Li(TFA)) precedes feeding guest material precursors (Yb(TFA)₃) as ScF₃ (Li⁺) and Yb³⁺, and the preparation of final products (ScF₃ (Li⁺) and Yb³⁺) is similar with that of products (ScF₃ and Li⁺/Yb³⁺), except that 1.5 mmol Li(TFA) is loaded into the reaction system at the first step rather than the second step.

Time-dependent reaction studies. 0.1 mL reaction mixture was extracted from the reaction flask at certain times. The sample mixtures were washed three times with cyclohexane and ethanol, and finally dispersed in 2 mL cyclohexane for further characterization.

In-situ **TEM** with heating holder. The as-obtained aliquots at 8 min was diluted to 10 mL and were transferred onto silicon nitride membranes which would be loaded into the holder after evaporation of cyclohexane. Once the loading process was finished, the holder was subsequently loaded into a JEOL JEM-2100F TEM operated at 200 kV.

Instrumentation. Samples for transmission electron microscopy (TEM) examination were prepared by drying a drop of the colloidal dispersion of NPs on a copper grid. TEM was

conducted with a JEOL JEM-2100 TEM operated at 200 kV. High resolution TEM (HRTEM), *in-situ* TEM, High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM), STEM-energy dispersive X-ray spectroscopy (EDS) line scan and selected area electron diffraction (SAED) measurements were performed with a JEOL JEM-2100F TEM operated at 200 kV. EDS elemental mapping was conducted on FEI Tecnai F30 operated at 300 kV. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2000 diffractometer (Japan), using Cu K α radiation ($\lambda = 1.5406$ Å). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was carried out with a Leeman Profile SPEC. Photoluminescence spectra were collected using an Edinburgh Instrument FLS980. The nanocrystal samples were diluted in cyclohexane and excited by a 980 nm laser optical fiber.

	a	b	с
Cubic ScF ₃	4.01 Å	4.01 Å	4.01 Å
Tetragonal LiYbF ₄	5.13 Å	5.13 Å	10.58 Å
Hexagonal NdF ₃	7.03 Å	7.03 Å	7.19 Å

Table S1. Lattice parameters of cubic ScF_3, tetragonal LiYbF_4, and hexagonal NdF_3.

Lanthanide fluorides have similar crystal structures to each other. Here tetragonal $LiYbF_4$ and hexagonal NdF_3 are chosen as the demonstrations to indicate the crystal structure differences among tetragonal $LiLnF_4$, hexagonal LnF_3 , and cubic ScF_3 .

Cubic	{110}	{210}	{100}
ScF ₃	d = 0.284 nm	d = 0.179 nm	d = 0.401 nm
Tetragonal	{204}	{204}	{101}
LiYbF ₄	d = 0.184 nm	d = 0.184 nm	d = 0.634 nm
facet	$ 2d_{110} - 3d_{204} /3d_{204} =$	$ d_{\{210\}} - d_{\{204\}} / d_{\{204\}} =$	$ 3d_{100} - 2d_{101} /2d_{101} =$
mismatch	2.90%	2.72%	5.13%
Hexagonal	{111}	{002}	{300}
NdF ₃	d = 0.316 nm	d = 0.360 nm	d = 0.203 nm
facet	$ d_{\{110\}} - d_{\{111\}} /d_{\{111\}} =$	$ 2d_{210} - d_{002} /d_{204} =$	$ d_{\{100\}} - 2d_{\{300\}} /2d_{\{300\}} =$
mismatch	10.1%	0.56%	0.99%

Table S2. The facet mismatch between cubic ScF_3 and tetragonal LiYbF₄ as well as hexagonal NdF₃.

Sample	[Yb]:[Sc]:[Li]
8 min	0.10:0.24:1.00
10 min	0.20:0.37:1.00
11.5 min	0.19:0.40:1.00
13.5 min	0.13:0.40:1.00
15 min	0.17:0.53:1.00
20 min	0.20:0.68:1.00
30 min	0.21:0.70:1.00
60 min	0.14:0.50:1.00

Table S3. ICP-AES element analysis of aliquots of reaction mixtures taken at different

reaction times



Figure S1. XRD patterns of samples extracted at different reaction times during the 320 °C. Standard cubic ScF_3 (ICDD: 00–046–1243) and tetragonal LiYbF₄ (ICDD: 01–071–1211) patterns are also shown.



Figure S2. Line scan files of samples acquired at 10 min.



Figure S3. HRTEM images of NCs with polycrystalline domains taken at 11.5 min.



Figure S4. TEM images of aliquots of reaction mixtures taken at 13.5 min. The blue stained part is cubic ScF_3 , the orange framed part is intermediates, and the blue frame part is poorly crystallized LiYbF₄.



Figure S5. The TEM images of products from a seed-growth method. (a) Seed NPs (seed 1) prepared with scandium precursors, (b) Seed NPs (seed 2) prepared with lithium and scandium precursors, (c) final NPs obtained by reacting seed 1 with addition of lithium and ytterbium precursors, (d) final NPs obtained by reacting seed 2 with addition of ytterbium precursors, (e) the HRTEM image of as-prepared products (ScF₃ and Li⁺/Yb³⁺) and (f) EDS line scan of a single ScF₃ nanoparticle from as-prepared products (ScF₃ and Li⁺/Yb³⁺).



Figure S6. Structure models of the atomic arrangement are constructed to further verify the possibility of the lattice match. The top views of structure models of the atomic arrangement in (a) the (204) plane of tetragonal LiYbF₄, (b) the (110) plane of cubic ScF₃ (top right). The side views of structure models of the atomic arrangement in (c) <020> of tetragonal LiYbF₄ and (d) <001> of cubic ScF₃.



Figure S7 The FFT patterns of the (a) ScF_3 -LiYbF₄ Janus nanoparticle, (b) LiYbF₄ and (c) ScF_3 domains.



Figure S8. The TEM images of as-prepared scandium fluoride–lanthanide fluoride Janus NPs, lanthanide = Dy, Tb, Eu, Sm, and Pr.



Figure S9. XRD patterns of ScF_3 - LiLnF₄ Janus NPs, Ln = Tb, Dy, and Lu. Standard cubic ScF_3 (ICDD: 00–046–1243), tetragonal LiTbF₄ (ICDD: 00–027–1262), orthorhombic TbF₃ (ICDD: 00–032–1290), tetragonal LiDyF₄ (ICDD: 00–027–1233), and tetragonal LiLuF₄ (ICDD: 00–027–1251) patterns are also shown in (a-c), respectively.



Figure S10. XRD patterns of ScF₃–LnF₃ Janus NCs, Ln = Pr, Nd, Sm, Eu, and Gd. Standard cubic ScF₃ (ICDD: 00-046-1243), hexagonal PrF₃ (ICDD: 00-078-1464), hexagonal NdF₃ (ICDD: 00-009-0416), hexagonal SmF₃ (ICDD: 00-012-0792), and hexagonal EuF₃ (ICDD: 00-032-0373) patterns are also shown. Since the XRD diffraction for the hexagonal GdF₃ was not documented, it is referred with hexagonal EuF₃ (ICDD: 00-032-0373).



Figure S11. TEM images of the temporal evolution for ScF_3 -NdF₃. (a) and (b), (c) and (d), (e) and (f), and (g) and (h) correspond to TEM image and HRTEM images of aliquots taken at 20.5 min, 23 min, 24.5 min, and 35 min. The portion in green frame is embryo, the portion stained by blue is cubic ScF_3 , the part stained by yellow is intermediate, and the purple stained part stands for hexagonal NdF₃.



Figure S12. TEM images of (a) Er^{3+} (2%), (b) Ho^{3+} (2%) and (c) Tm^{3+} (0.5%) doped ScF₃-LiYbF₄ NPs.



Figure S13. Normalized upconversion emission spectra of as-prepared (a) Er^{3+} (2%), (b) Ho^{3+} (2%), and (c) Tm^{3+} (0.5%) doped ScF₃–LiYbF₄ Janus NPs. NPs are irradiated by 980 nm laser (24 W/cm²).