Electronic Supplementary Information:

Raisinlike rare earth doped gadolinium fluoride nanocrystals: microwave synthesis, and magnetic and upconversion luminescent properties

Song Wang,[ab] Shengqun Su,[a,b] Shuyan Song,[a] Ruiping Deng[a] and Hongjie Zhang[a*]

State Key Laboratory of Rare Earth Resource Utilizations,
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,
Changchun, 130022, Jilin, China.
E-mail: hongjie@ciac.jl.cn; Fax: +86 431 8569 8041;
Tel: +86 431 8526 2127
Graduate School of the Chinese Academy of Sciences, Beijing, 100039,
P. R. China

1. Experimental procedures

1.1 Synthesis

All the chemicals were of analytical grade and used as received without further purification. $Gd(NO_3)_3$, $Er(NO_3)_3$, $Yb(NO_3)_3$, $Ho(NO_3)_3$, $Er(NO_3)_3$ aqueous solution were obtained by dissolving $Gd(NO_3)_3{\cdot}6H_2O$(99.9%), $Er(NO_3)_3{\cdot}6H_2O$ (99.9%), $Yb(NO_3)_3{\cdot}6H_2O$ (99.9%), $Yb(NO_3)_3{\cdot}6H_2O$ (99.9%), $Yb(NO_3)_3{\cdot}6H_2O$ (99.9%) in deionized water, respectively.

All the synthesis processes were performed on a programmed microwave synthesis reactor(START SYNTH, Milestone), which is equipped with inner symmetrical quartz tubes. The tubes were located on a rotated plate, which make all the reaction in the same condition. The temperature was monitored by an inner IR detector. All the reaction parameters were programmed with optimized increased time, target temperature, standing time and temperature. For a typical experiment, 1 mmol $NaBF_4$ was added to 10 mL aqueous solution containing 0.1 mmol $Gd(NO_3)_3$ under vigorous stirring and the system was additional stirred for 10 min. The resultant solution was transferred to the quartz tubes and located in the reactor, then set parameters are as follows: microwave irradiation power 200 W, increasing time 5 min, target temperature 85 ℃,standing time 5 min, standing temperature 85 ℃. Finally, the quartz tubes were cooled to room temperature naturally. The precipitates were separated by centrifugation, followed by washed with deionized water for 3 times. The final product was dried at 80 ^oC in air for about 12 h. The Ln^{3+}-doped GdF_3 microflowers were prepared by the same procedure, except for adding corresponding relevant Ln^{3+} (Ln^{3+} = Yb^{3+} and Er^{3+}) into the solution of $Gd(NO_3)_3$ at the initial stage. To improve the crystallinity of the nanocrystalline powder, the resultant product was annealed at 400 ^oC for 4h.

1.2 Characterization

The crystalline and phase purity of the products were examined by powder XRD. Measurements were performed on a Rigaku X-ray diffractometer with Cu Ka radiation with an accelerating voltage and applied current of 40 kV and 40 mA, respectively. The size, general morphology and structure of the as-synthesized samples were characterized using field-emission scanning electron microscopy (SEM) (Hitachi S4800) at an accelerating voltage of 10 kV and Hitachi 8100 transmission electron microscope (TEM) at an operation voltage of 200 kV. The UC

spectra were obtained by using a 980 nm laser diode. The emission attributed to the transitions between 350 and 850 nm was dispersed by a triple grating monochromator (Spectra Pro-2758, Acton Research Corporation, USA) equipped with a Photomultiplier (Hamamatsu R928). The ZFC and FC magnetization curves in a temperature range between 2 and 300 K at a 100 Oe applied field and the magnetization as a function of the applied field at temperature 2 K and 300 K in field between -60 and 60 kOe have been measured using a Quantum Design MPMS-7 SQUID magnetometer.

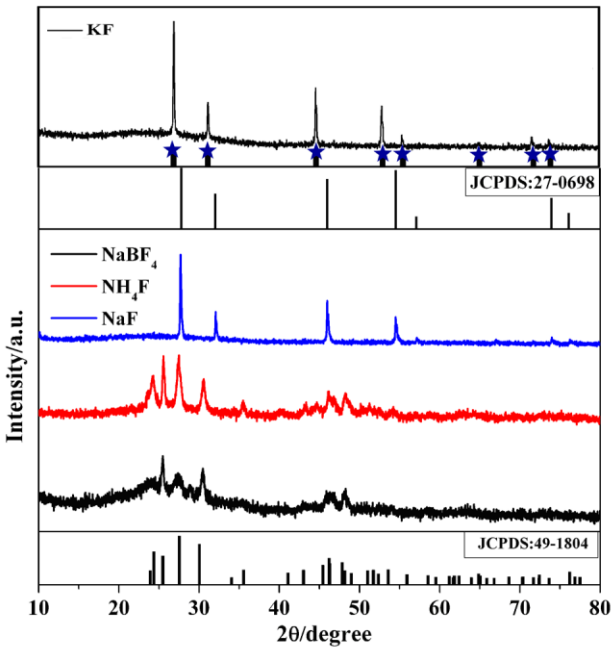

Fig. S1 XRD patterns of the as-prepared samples by using different precipitator before calcinations the corresponding standard pdf card.

Compared to the standard PDF data, the XRD patterns of the as-prepared sample predicated by KF are similar to those of pure cubic phase α-$NaGdF_4$ (space group: *Fm-3m*). Indexing the diffraction peaks indicates a cubic unit cell with lattice constants a = 5.74 Å. Based on this value, we simulated the diffraction peaks based on the crystallographic data of cubic $KGdF_4$ by employing the MDI JADE 5.0 software according to the reference[1]. The positions of calculated diffraction peaks (blue star in Fig. 1) are consistent with the experimental results.

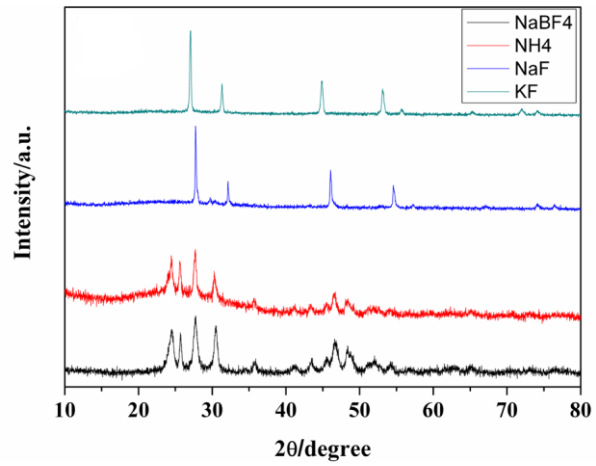

Fig. S2. XRD patterns of the as-prepared samples by using different precipitator after calcinations

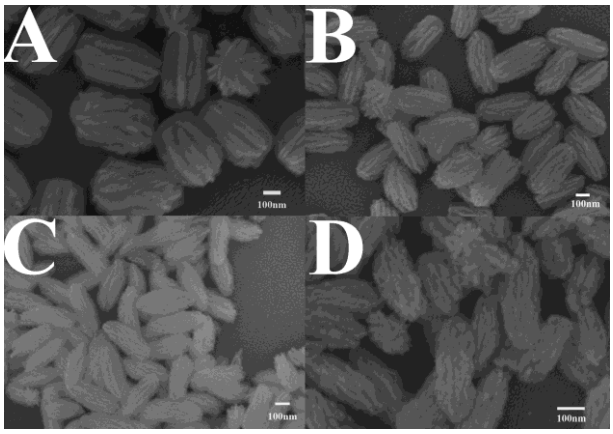

Fig. S3. SEM images of raisin like GdF_3 nanocrystals by using different amount $NaBF_4$: (A) 0.3 mmol, (B) 0.6 mmol, (C) 1 mmol, (D) 2 mmol.

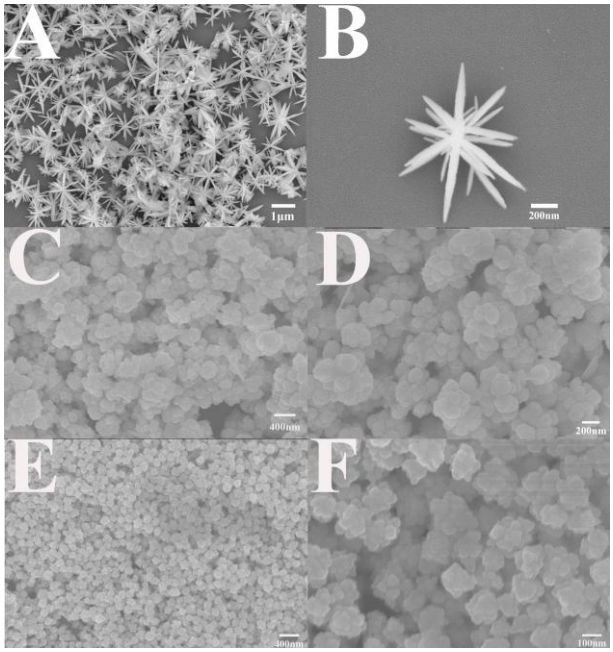

Fig. S4 Low- and high-magnification SEM images of samples obtained by using different precipitators: (A) and (B) NH4F, (C) and (D) NaF, (E) and (F) KF.

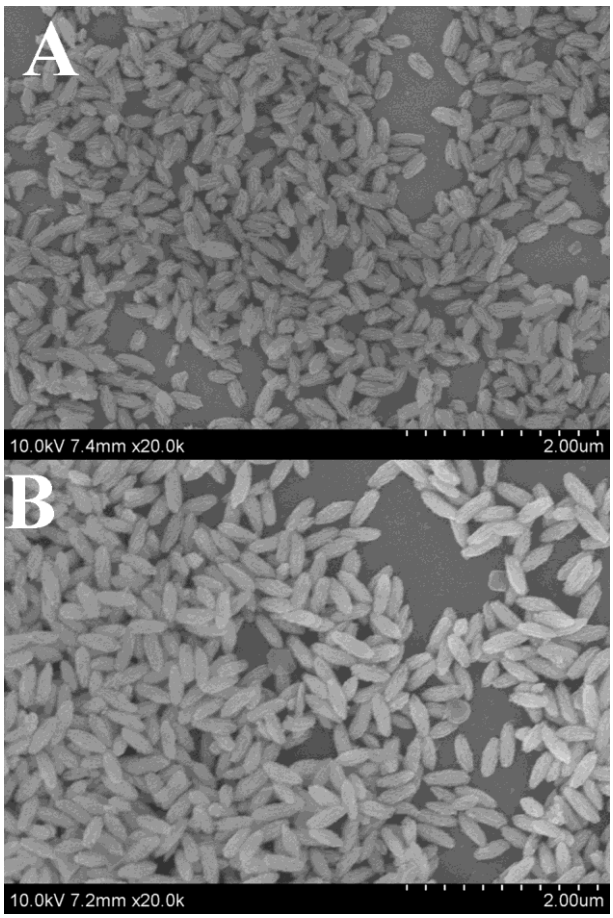

Fig.S5 (A) SEM images of raisin like GdF_3 nanocrystals before (A) and after calcinations (B).

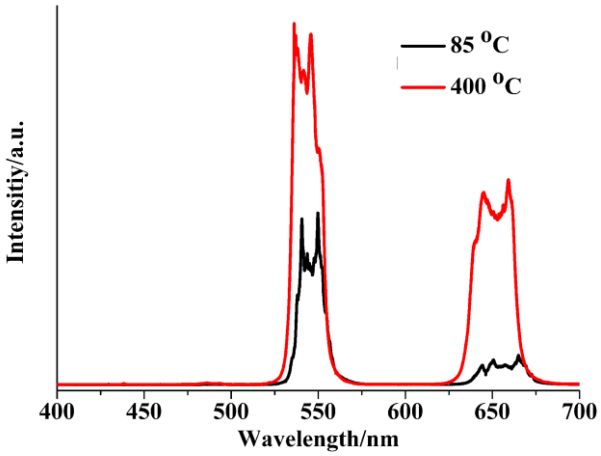

Fig. S6 Upconversion spectra of the raisin-like GdF_3:20%Yb^{3+}/2%Ho^{3+} nanocrystals before and after calcinations.

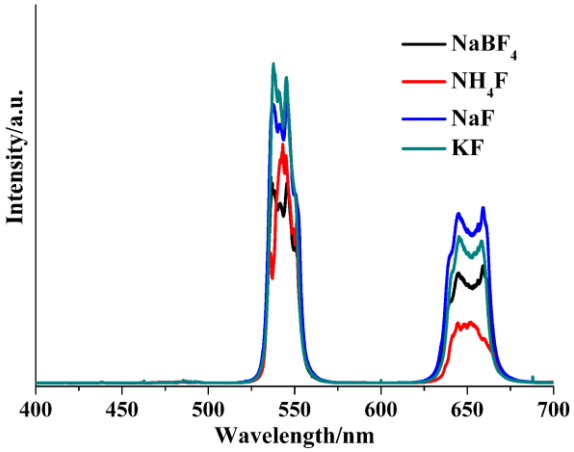

Fig. S7. Upconversion spectra of the as prepared samples by using different precipitators.

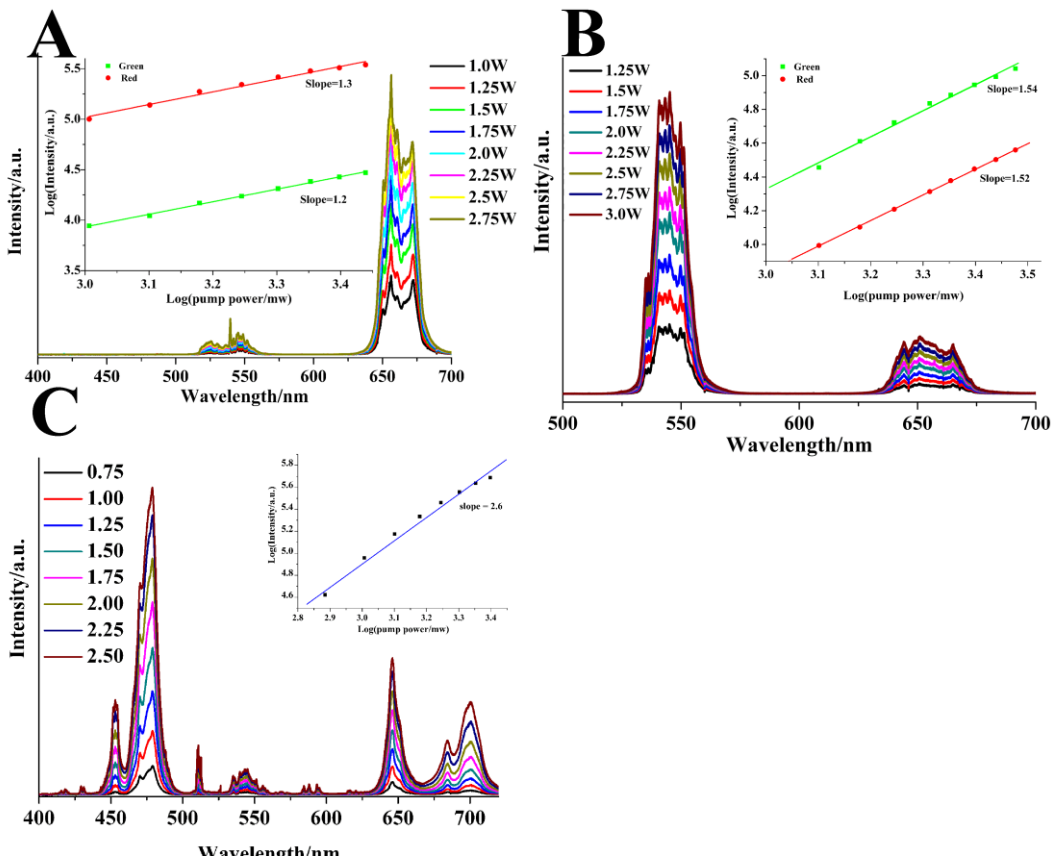

Fig. S8 Power dependent upconversion spectra and log-log plot of the raisin-like RE doped GdF3 nanocrystals: (A) GdF_3:20%Yb^{3+}/2%Er^{3+} (B) GdF_3:20%Yb^{3+}/Ho^{3+} (C) GdF_3:10%Yb^{3+}/0.5%Tm^{3+}

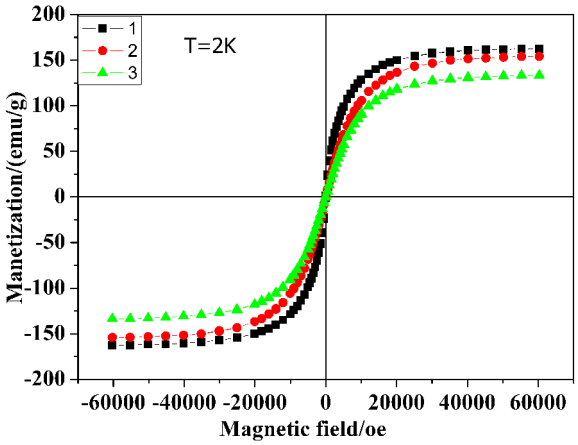

Fig. S9. Magnetization vs magnetic field of the raisin like (1)GdF_3 (2) GdF_3:10%Yb^{3+}/Ho^{3+} and (3) GdF_3:20%Yb^{3+}/Ho^{3+} sub-microcrystals at 2 K.

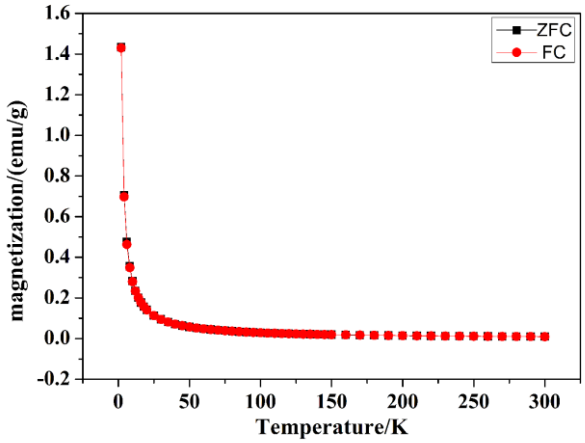

Fig. S10 Temperature dependence of ZFC-FC magnetization of the GdF_3 nanocrystals

Notes and references

1 L. W. Yang, Y. Y. Zhang, J. J. Li, Y. Li, J. X. Zhong and Paul K. Chu Nanoscale, 2010, 2, 2805.