Electronic Supplementary Material (ESI) for Dalton Transactions.

pH value manipulated phase transition, microstructure evolution and tunable upconversion luminescence in Yb^{3+}-Er^{3+} codoped $LiYF_4/YF_3$ nanoparticles

Song Ye[1,*], Rongxuan Hu[1], Nan Jiang[2], Huiyun Wang[1] and Deping Wang[1]

1. School of Materials Science and Engineering, Tongji University, Shanghai 201806 China

2. Department of Physics, Arizona State University, Tempe, AZ 85287-1504, USA

Email: yesong@tongji.edu.cn

Supporting Information

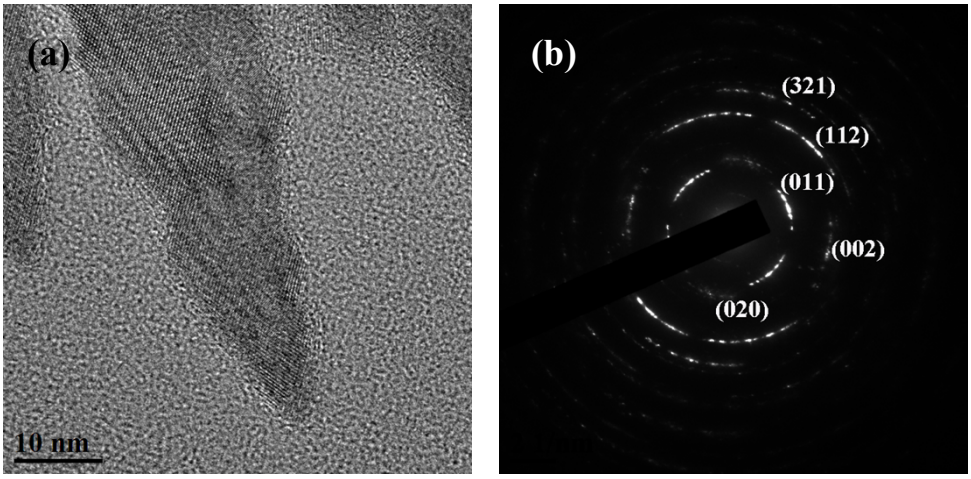

Fig. S1 HRTEM image of the YF_3: Er^{3+}, Yb^{3+} nanocrystals synthesized with mother solution pH value of 3.90 (a) and the corresponding selected area electron diffraction (SAED) pattern (b)

A tip in a single petal-like substructure was selected to take the HRTEM measurement, as shown in Fig. S2(a), from which the lattice fringes can be clearly observed. The SAED pattern in Fig. S2 (b) shows spotty polycrystalline diffraction rings corresponding to the (011), (020), (002), (112) and (321) planes of YF_3, which conformed the bowknot-like nanostructure is YF_3 crystal.

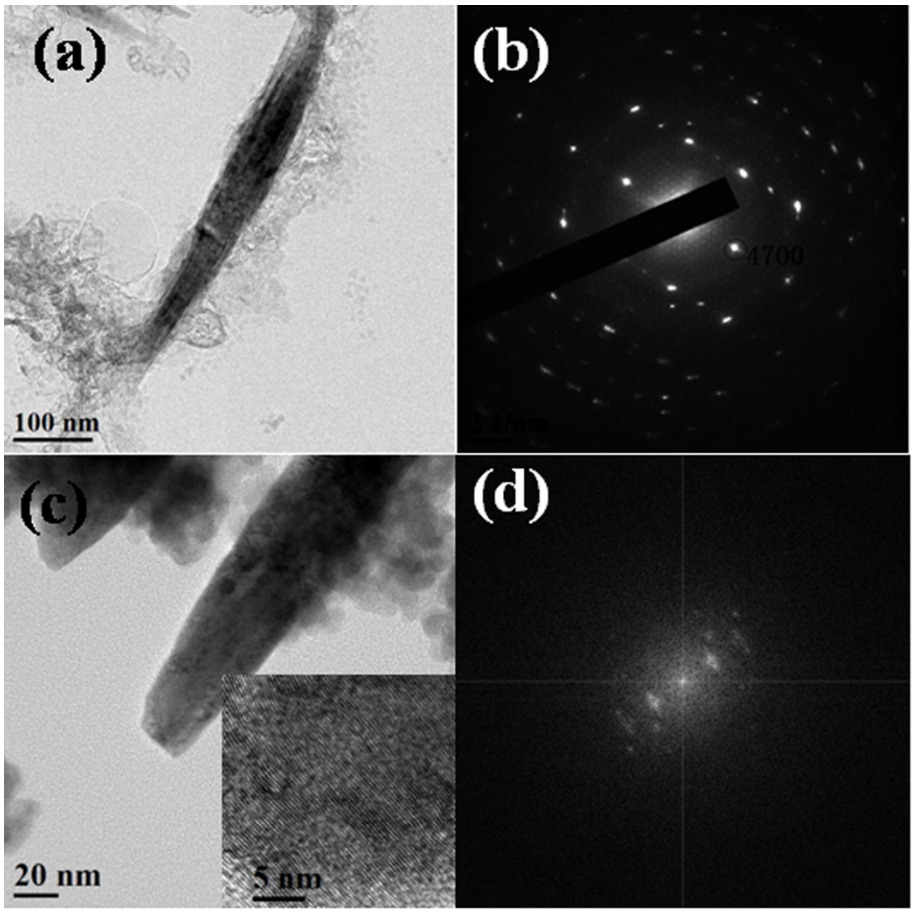

Fig. S2 TEM image (a) and the corresponding selected area electron diffraction (SAED) pattern (b) for the intermediates obtained under pH value of 3.90 after 2h of reaction; TEM image (c) and the FFT image (d) for the intermediates obtained under pH value of 2.00 after 2h of reaction. The inset in Fig S2(c) show the HRTEM image of the "spindle" tips.

With mother solution pH value of 3.90, the YF_3 single nanobelts were formed after 2h of reaction. According to the SAED pattern, the preferential growth orientation of the YF_3 nanobelts is [100]. These nanobelts may self assembled into the bowknot-like structure with prolonged reaction, as shown in Fig. 2 (d-e).

While under mother solution pH value of 2.00, the loose spindle-like YF_3 nanoparticles begin to form with 2h of reaction. It is indicated from the HRTEM and the corresponding FFT images that the preferential growth orientation of the YF_3 spindle is [111].

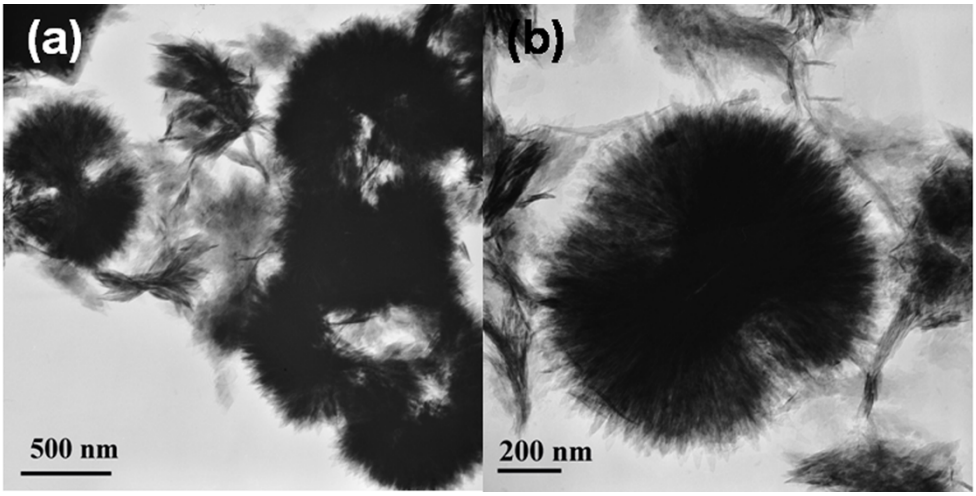

Fig. S3 TEM images of YF_3 nanoparticles synthesized under pH value of 3.90, the starting concentrations of LiOH, $Ln(NO_3)_3$ (Ln=Y, Yb and Er) and NH_4F are 4M .

In order to investigate effect of initially formed YF_3 nanobelt concentration on the final morphology of the assembled YF_3 bowknot, the YF_3 nanoparticles were synthesized under pH value of 3.90 by taking the same procedure described in the Experimental part, however, the starting concentrations of LiOH (4M), $Ln(NO_3)_3$ (4M, Ln=Y, Yb and Er) and NH_4F (4M) are doubled. The TEM images for the final product are shown in Fig. S3. Compared with the TEM images in Fig. 2 (d-e), it can be clearly observed that with more YF_3 nanobelt as the supplier, the YF_3 bowknots with more open ends are formed during the self- assemble process with prolonged reaction, and some of them are even approaching to a sphere structure. This experiment result proved that the higher the initial formed YF_3 nanobelts concentration, the more open ends the bowknot-like structure will has.

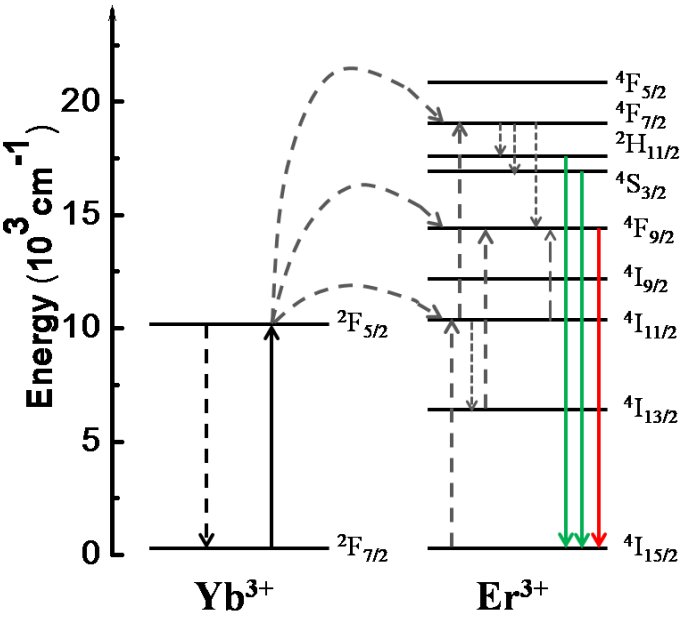

Fig. S4 Energy level diagram that describes the upconversion luminescence mechanisms of Yb^{3+}-Er^{3+} couple. .

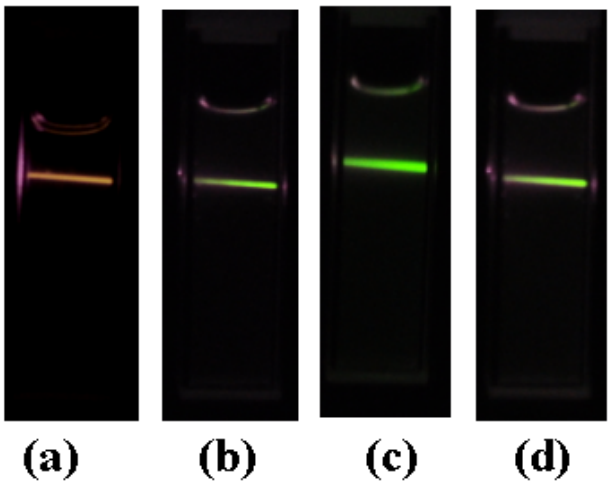

Fig. S5 shows the photographs of the visible upconversion emission in the 0.2wt% acetone solutions of Yb^{3+}-Er^{3+} codoped nanoparticles synthesized with different mother solution pH values of 6.20 (a), 4.20 (b), 3.90 (c) and 3.60 (d), respectively, under 980nm laser excitation. The upconversion emission intensity in the Yb^{3+}-Er^{3+} codoped nanoparticles synthesized with pH value of 3.90 is the strongest one, and the red to green emission intensity variation also can be clearly observed.