Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of a novel bifunctional nanocomposite with tunable upconversion emission and magnetic properties

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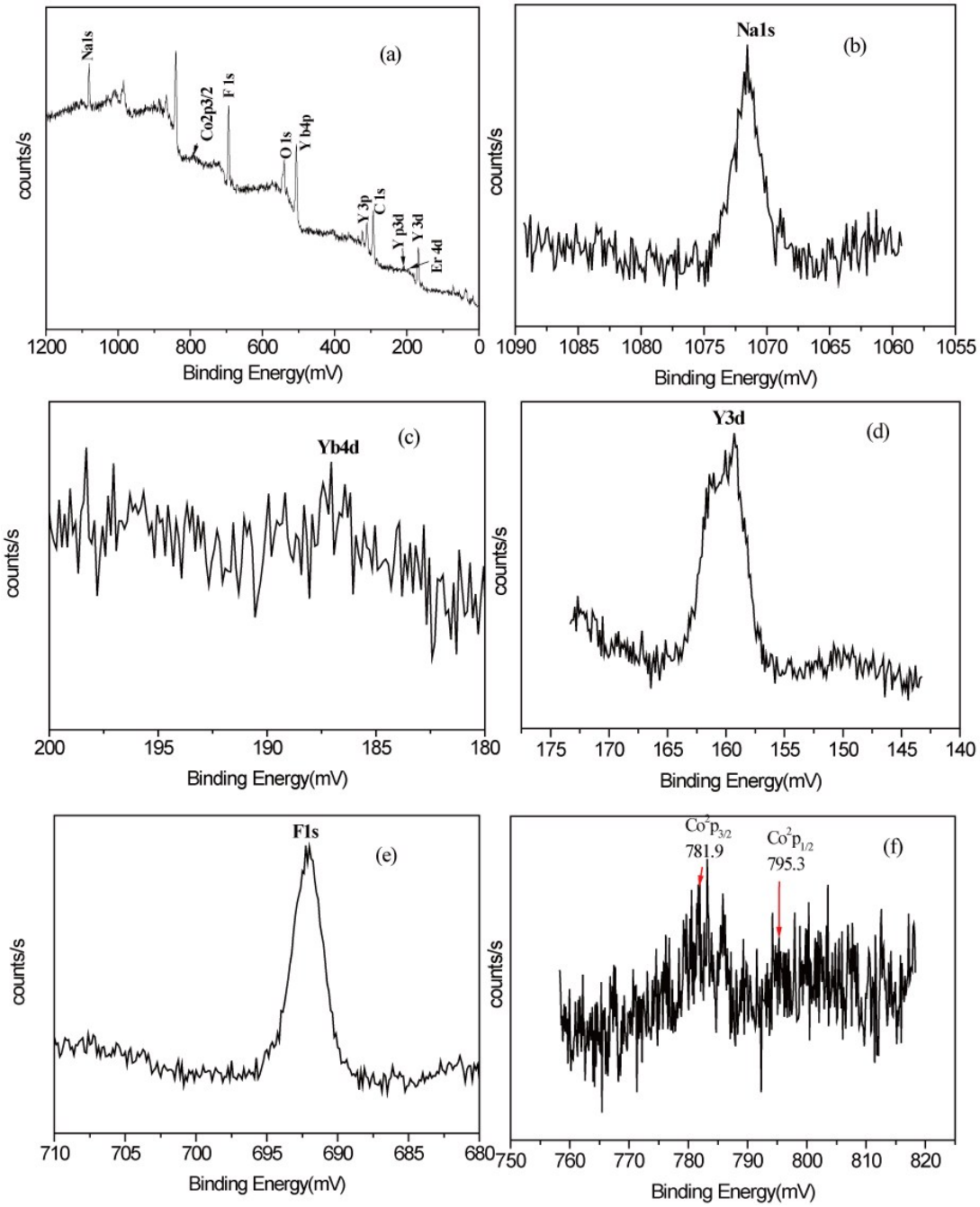

Fig.S1. (a) XPS spectrum of 30 mol% Co^{2+}-doped $NaYF_4$: Yb^{3+}/Er^{3+} (20/2 mol%); (b)，(c)，(d)，(e)，(f) The expanded spectrum of Na1s, Yb4d, Y3d, F1s and Co 2p. The Co 2p1/2 and 2p3/2 signals are located at 789.0 and 795.3 eV, respectively. These values agree well with literature values of Co^{2+} ions

To confirm further the chemical bonding states of Co ions in the doped

$NaYF_4$:Yb^{3+}/Er^{3+} NPs, X-Ray photoelectron spectroscopy (XPS) measurements were carried out on the sample with 30 mol% Co^{2+} ions codoping. The XPS survey spectrum (Fig.S1.a) shows the presence of Na, Y, F, Yb, Er and Co elements. Fig.S1. f shows the high resolution Co 2p spectrum of 30 mol% Co codoping in $NaYF_4$ Yb^{3+}/Er^{3+} sample. There are two main peaks, positioned at the binding energy sites of 781.9 eV and 795.3 eV, corresponding to the Co $^2p_{3/2}$ and Co $^2p_{1/2}$ orbitals, respectively. A report state that the Co $^2p_{3/2}$ peak corresponding to the Co-Co bonding was located at 778.1-778.3 eV, and the peak corresponding to the Co-F bonding was located around 780eV. Therefore, Co ions, in the +2 oxidation state, are surrounded by F ions, that is, Co^{2+} successfully substituted for Y^{3+} in the $NaYF_4$ lattice[1] In addition, it can be seen that the binding energy (calibrated using C 1s (284.7 eV) as the reference) of Y (Y3p3/2, 316 eV; Y3p3/2, 304 eV; 3d5/2, 159.6 eV), Na (1s, 1074 eV), F(1s, 692 eV), Yb (4d, 196 eV) and Er (4d, 176 eV) are obvious (the C signal is due to the carbon used as reference). In Fig.S1. (a), there are one peak positioned at the binding energy sites of 538.8 eV, corresponding to the O in the OA on the surface of the nanoparticles.

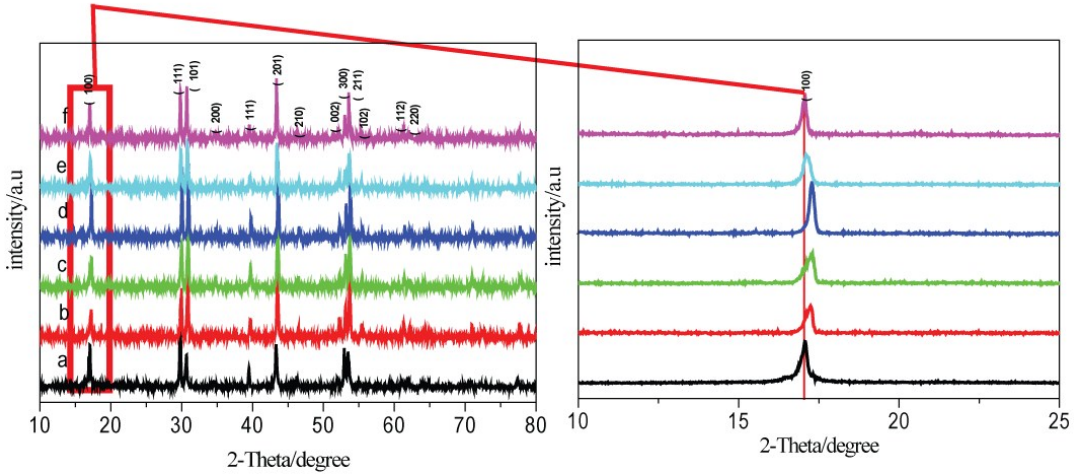

Fig.S2. XRD patterns of $NaYF_4$ samples codoped with different Co^{2+} ions concentration: (a) 0%, (b) 5%, (c) 10%, (d) 15% (e) 20% and (f) 30%.

Fig.S2. shows that Co^{2+} ions codoping do not induce the hexagonal phase transformation. The pure hexagonal $NaYF_4$ NPs were obtained even the Co^{2+} ions concentration increased to 30 mol%, indicating all the Co^{2+} ions were incorporated into the host matrix and formed a Y-Co solid solution structure. The enlarged area shows that all the diffraction peaks (100) shift slightly to larger angles for Co^{2+} ion concentration of 0-15 mol%, then gradually move reversely for Co^{2+} ion concentration of 15-30 mol% as a result of changing the unit-cell volume due to the substitution or occupation of Y^{3+} ions by small Co^{2+} ions in the host lattice.

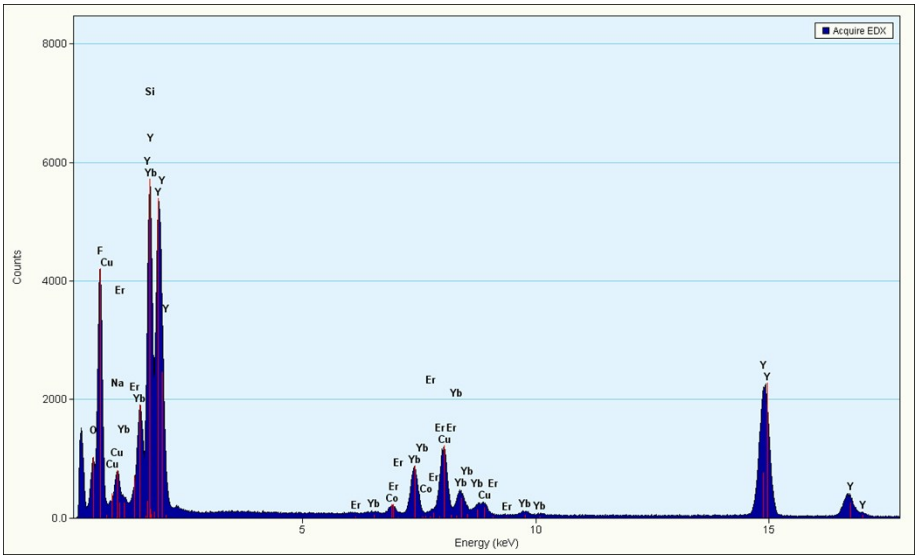

Fig.S3. EDX pattern of the 30 mol% Co^{2+}-doped $NaYF_4$: Yb^{3+}/Er^{3+} NPs reveal the existence of the dopant elemental Co.

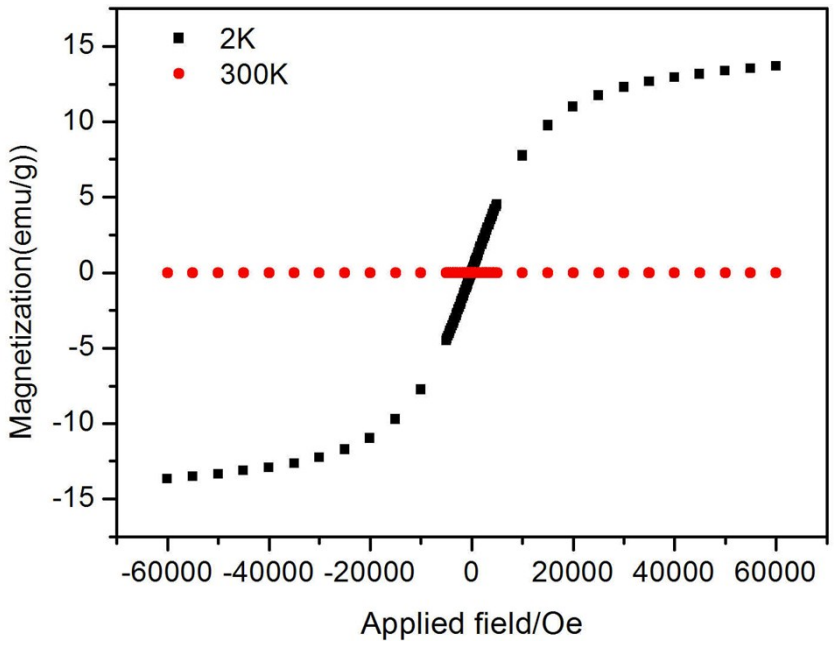

Fig.S4. M(H) measurements at 2 and 300K of 30 mol% Co-doped $NaYF_4$:Yb^{3+}/Er^{3+} NPs.

Fig.S4 shows the M(H) measurements at 2 and 300K of 30 mol% Co-doped $NaYF_4$:Yb^{3+}/Er^{3+} NPs. Typital superparamagnetism behavior is observed at 2K due to the absence of remanence(Mr) or coercivity(Hc), and the saturation magnetization(Ms) is approximately 13.77emu/g for the sample of 30% Co^{2+} doped $NaYF_4$: Yb^{3+}/Er^{3+}

NPs. However, all the samples shows a purely paramagnetic behavior at room temperature, indicating that the Curie temperature (*Tc*) is below 300K.[2]

Notes and references:

1.H. J. Hao, M. Qin and P. Li, *J Alloy Compd*, 2012, **515**, 143.

2. D. Santos and M. A. Macedo, *Physica B*, 2012, **407**, 3229.