

Supporting Information: ITO nanoparticles enhanced upconversion luminescence in Er³⁺/Yb³⁺ codoped silica glasses

I . Supplementary Methods

Materials.

All reagents and solvents are commercially available and were used as received without further purification. Silicon dioxide (SiO₂, 99.99%), boric acid (H₃BO₃, 99.99%), sodium carbonate anhydrous standard (Na₂CO₃, 99.999%), aluminium hydroxide (Al(OH)₃, 99.99%), indium (III) chloride tetrahydrate (InCl₃ • 4H₂O, 99.99%), tin (IV) chloride pentahydrate (SnCl₄ • 5H₂O, 99.995%), erbium (III) nitrate pentahydrate (Er(NO₃)₃•5H₂O, 99.9%) and ytterbium (III) nitrate pentahydrate (Yb(NO₃)₃•5H₂O, 99.99%) were purchased from Aladdin reagent. During the whole experiment process, deionized water was used.

Detail about the host silicate glass.

The typical composition of the bulk porous glass is 60SiO₂ • 25B₂O₃ • 5Al₂O₃ • 10Na₂O (wt %). The material is melted at 1500 °C, then cooled and annealed. The annealed bulk glass is processed into glass rods with diameter of 3.5 mm. And the later preparation of the mesoporous silica glasses followed the process described in our previous reports¹⁻⁴. After processing, we finally got the pure silica glass matrix.

Synthesis of Er³⁺/Yb³⁺ and ITO NPs codoped silica glass.

The glass samples were synthesized by an in-situ formation with a heat treatment followed. As shown in Table S1 and Table S2, different concentrations of InCl₃•4H₂O, SnCl₄•5H₂O were introduced in the glass with the same concentrations of

$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Porous silica glasses with the pore size around 5-40 nm was immersed into the solutions as listed in Table S1 and Table S2 respectively, the solvents are all deionized water. After about 24h, the glasses doped with different solutions were dried in super-clean air for about 2h, followed by a sintering process in air to above 1000 °C in order to make the ITO NPs grow and collapse the nanoporous structure. Finally, the glass samples were polished to meet the requirements for optical measurements.

Characterization.

Samples were characterized by the X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda=0.154\text{nm}$) at scanning speed of 5 degree per minute in the range from 10° to 70° and the Tecnai G20 U-Twin Transmission Electron Microscope (TEM). The absorption spectra were collected with the UV3600 spectrophotometer. The luminescence spectra were collected with the Zolix spectrofluorimeter upon excitation of a 980 nm laser diode.

II. Supplementary Tables

Table S1. Dopants Concentration of the synthesized samples with different concentration of ITO NPs

Samples	dopants (mol/L)			
	$\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	$\text{InCl}_3 \cdot 4\text{H}_2\text{O}$	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
ITO 0	0.5	0.1	0	0
ITO 0.2	0.5	0.1	0.2	0.02
ITO 0.4	0.5	0.1	0.4	0.04
ITO 0.6	0.5	0.1	0.6	0.06
ITO 0.8	0.5	0.1	0.8	0.08
ITO 1.0	0.5	0.1	1.0	0.1

Table S2. Dopants Concentration of the synthesized samples with different Sn to In atom ratios

Samples Sn:In	dopants (mol/L)			
	$\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	$\text{InCl}_3 \cdot 4\text{H}_2\text{O}$	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
0:0	0.5	0.1	0	0
100:0	0.5	0.1	0	0.4
80:20	0.5	0.1	0.08	0.32
60:40	0.5	0.1	0.16	0.24
40:60	0.5	0.1	0.24	0.16
20:80	0.5	0.1	0.32	0.08
0:100	0.5	0.1	0.4	0

III. Supplementary Figures

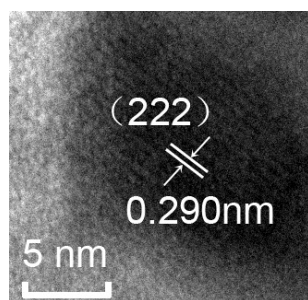


Figure S1. The HR-TEM micrograph of ITO NP in ITO 0.4

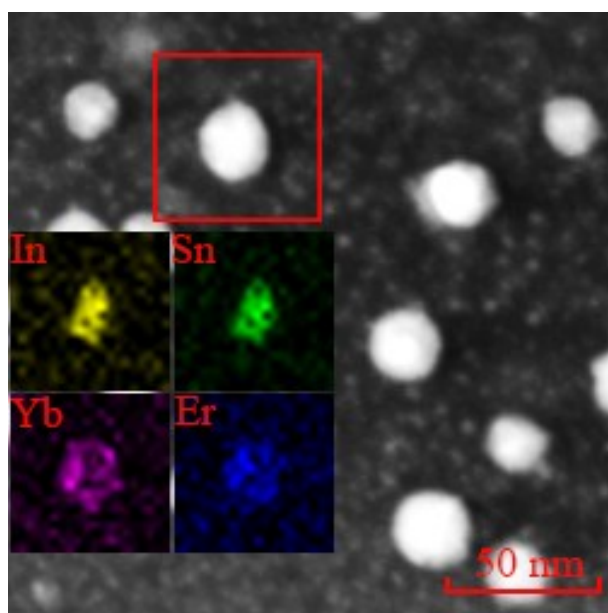


Figure S2. TEM mapping images of ITO 0.4

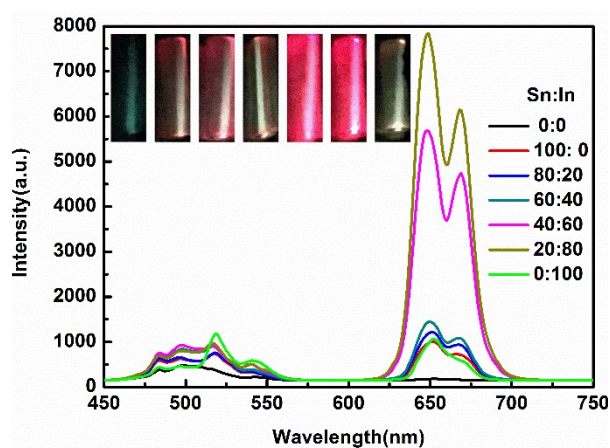


Figure S3. UC emission spectra of $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped silica glasses samples with different Sn to In atom ratios under identical experimental conditions at room temperature under 980 nm excitation and fluorescence photographs (left to right)

corresponding to all samples (inset) (ratios from 0:0 to 0:100) respectively

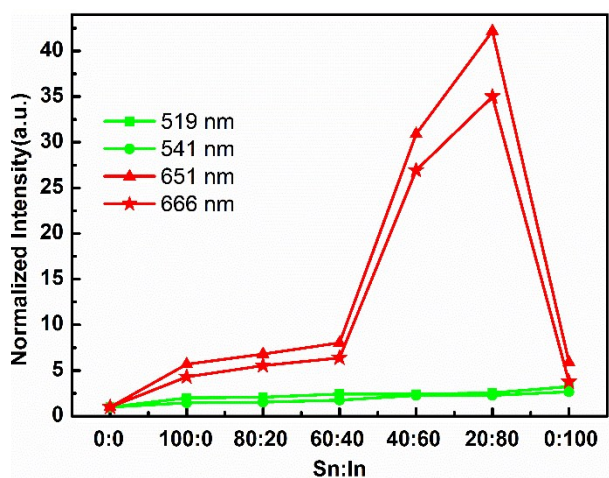


Figure S4. Relationship between the normalized intensity of UC emission (F/F_0) and the Sn to In atom ratios at 519 nm, 541nm, 651 nm, 666 nm, respectively

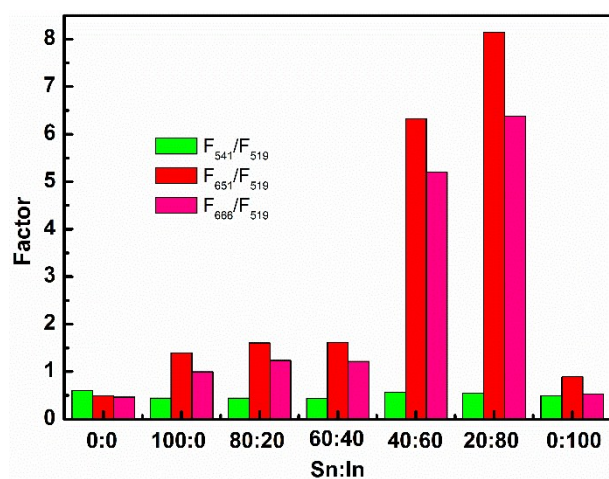


Figure S5. F_{541}/F_{519} , F_{651}/F_{519} , F_{666}/F_{519} versus the Sn to In atom ratios

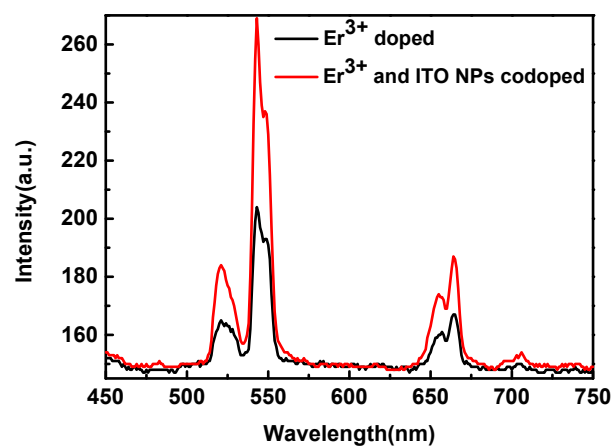


Figure S6. UC emission spectra of Er^{3+} (0.1 mol/L) doped silica glasses samples with

and without ITO NPs (0.4 mol/L) under identical experimental conditions at room temperature under 980 nm excitation

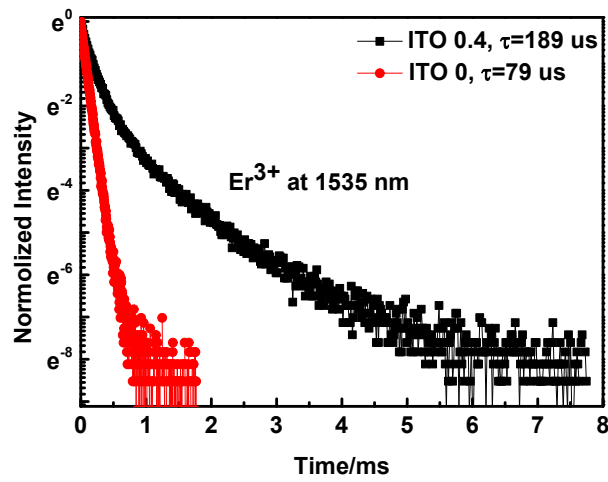


Figure S7. Time-resolved spectra of ITO 0 and ITO 0.4 in Table S1 at room temperature under 980 nm excitation at 1535 nm

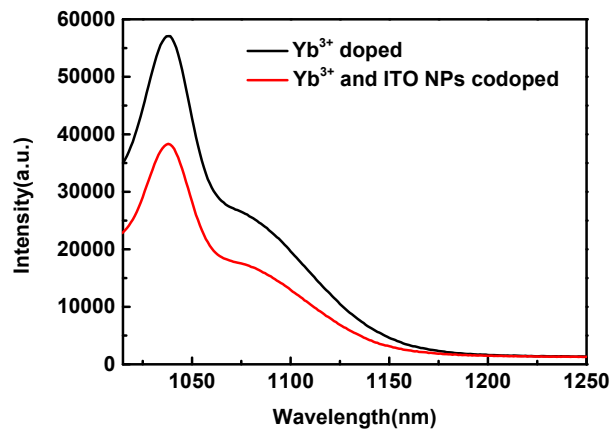


Figure S8. Emission spectra of Yb^{3+} (0.5 mol/L) doped silica glasses samples with and without ITO NPs (0.4 mol/L) under identical experimental conditions at room temperature under 980 nm excitation

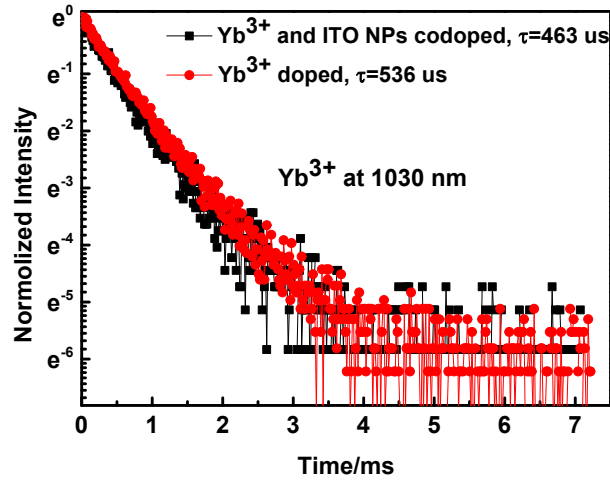


Figure S9. Time-resolved spectra of Yb^{3+} (0.5 mol/L) doped silica glasses samples with and without ITO NPs (0.4 mol/L) at room temperature under 980 nm excitation at 1030 nm

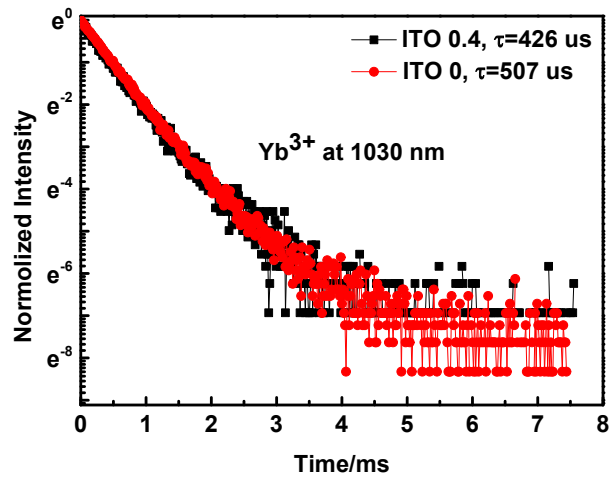


Figure S10. Time-resolved spectra of ITO 0 and ITO 0.4 in Table S1 at room temperature under 980 nm excitation at 1030 nm

1. D. Chen, H. Miyoshi, T. Akai and T. Yazawa, *Applied Physics Letters*, 2005, **86**, 231908.
2. Z. Liu, N. Dai, H. Luan, Y. Sheng, J. Peng, Z. Jiang, H. Li, L. Yang and J. Li, *Optics express*, 2010, **18**, 21138-21146.
3. L. Yang, M. Yamashita and T. Akai, *Optics express*, 2009, **17**, 6688-6695.
4. L. Yang, N. Dai, Z. Liu, Z. Jiang, J. Peng, H. Li, J. Li, M. Yamashita and T. Akai, *Journal of Materials Chemistry*, 2011, **21**, 6274.