

Supporting information

Strong up-conversion luminescence of rare-earth doped oxide films enhanced by gap modes on ZnO nanowires

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1. Experimental Details

Materials. All chemicals were obtained from commercial suppliers and used without further purification. Rare-earth nitrates, erbium nitrate ($\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%), thulium nitrate ($\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%), and ytterbium nitrate ($\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%) were purchased from Aladdin Chemistry Co Ltd in Shanghai, China. Ammonium paramolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\geq 99\%$), sodium hydroxide (NaOH, $\geq 98\%$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, $\geq 99\%$) were purchased from Sinopharm Chemical Reagent Co Ltd in Shanghai, China. The sputtering targets of Ag (99.99%) and ZnO (99.99%) were purchased from ZhongNuo Advanced Material (Beijing) Technology Co Ltd with the diameter of 80 mm.

Synthesis of Ag layer, ZnO seed, and ZnO film. The glasses substrates were washed with a freshly prepared mixed solution H_2SO_4 (98%): H_2O_2 (33%) in a 3:1 ratio by volume, followed by rinsing with copious amounts of deionized water. A high-vacuum duplex chamber sputtering apparatus was used for the deposition of Ag layer, ZnO seed, and ZnO film. Firstly, the glasses substrates were cleaned by RF sputtering in the sampling chamber with the Ar pressure of 8 Pa for 10 min. Then Ag layer was deposited by direct-current (DC) magnetron sputtering, and ZnO seed and ZnO film were deposited by radio-frequency (RF) magnetron sputtering. Detailed parameters were showed in Table S1.

Synthesis of nw-ZnO layer. The hydrothermal process was used to grow nw-ZnO layer based on the ZnO seed. Firstly, a ZnO seed layer was prepared as above. After a calcination treatment in air at 573 K for 30 min to obtain crystallized ZnO seed layer,

the substrates were then placed into a Teflon-lined autoclave which contained an aqueous solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (35 mM) and $\text{C}_6\text{H}_{12}\text{N}_4$ (35 mM). The autoclave was sealed and heated to 368 K, and the reaction continued for 2 h. The nw-ZnO layer with various lengths can be obtained by change the reaction time from 0.5 h to 5 h. Then, the samples were rinsed with deionized water to remove particles and dried in the vacuum oven.

Synthesis of $\text{Er}^{3+}(\text{Tm}^{3+})$ doped YbMoO_4 layer. The detailed synthesis procedure was as follows: 0.0443 g $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (or 0.0089 g $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and 0.4492 g $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were first dissolved in 5 ml absolute ethyl alcohol to obtain solution A. Then 0.7415 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 10 ml of deionized water to yield solution B, the pH value of the solution B was adjusted to 7.0 using 1 M NaOH solution. A spin-coating technique was used to prepare the rare-earth doped oxide layer. Firstly, solution A was dripped on the substrate and, after left undisturbed for 60 s, the substrate was spun at the speed of 2500 rpm for 30 s. Then, solution B was dripped rapidly and left undisturbed for 60 s, subsequently the substrate was spun at the speed of 2500 rpm for 30 s. The above-prepared samples were annealed at the heating rate of 3 K/min, kept at the annealing temperature of 773 K for 2 h, and then cooled down to room temperature inside the furnace.

2. Supplementary Tables and Figures

Table S1. Parameters of magnetron sputtering for the deposition of Ag layer, ZnO seed, and ZnO film.

| Sputtering items | Parameters for Ag layer | Parameters for ZnO seed | Parameters for ZnO film |
|------------------------------|-------------------------|-------------------------|-------------------------|
| Target to substrate distance | 70 mm | 70 mm | 70 mm |
| Sputtering power | 60 W | 60 W | 80 W |
| Process gas | 99.99% Ar | 99.99% Ar | 99.99% Ar |
| Working pressure | 0.3 Pa | 0.3 Pa | 0.5 Pa |
| Deposition time | 80 s | 240 s | 10800 s |
| Film thickness | 28 nm | 5 nm | 540 nm |

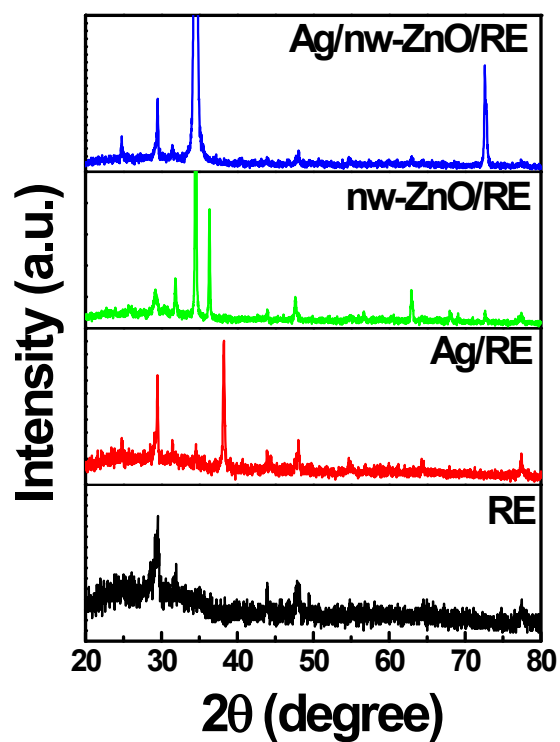


Figure S1. XRD patterns of RE, Ag/RE, nw-ZnO/RE, and Ag/nw-ZnO/RE composite films.

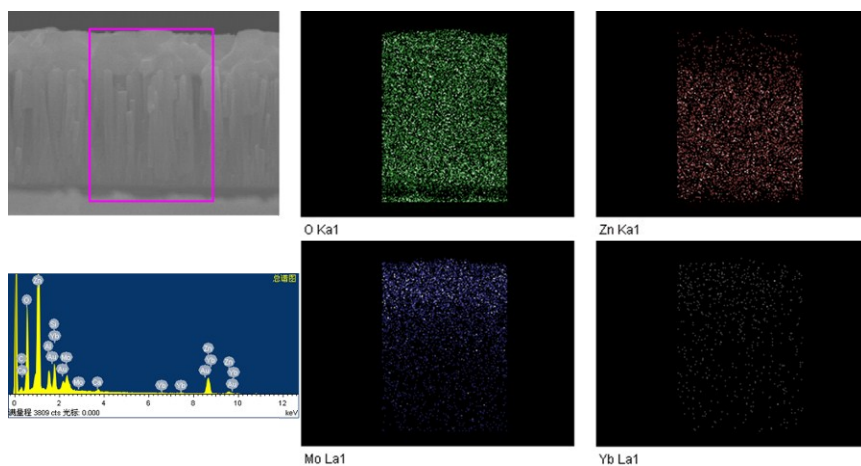


Figure S2. Energy Dispersive X-Ray (EDX) element mapping and spectrum of the Ag/nw-ZnO/RE composite film.

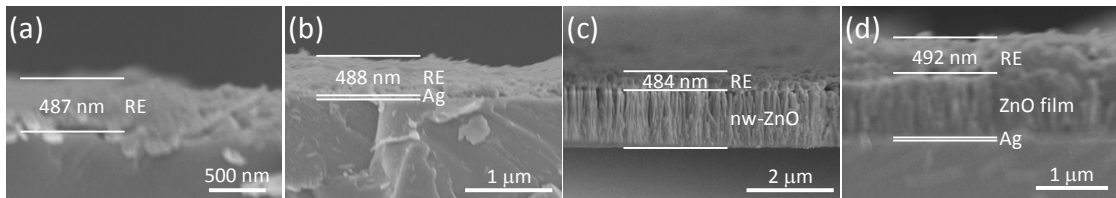


Figure S3. Cross-sectional SEM images of (a) RE, (b) Ag/RE, (c) nw-ZnO/RE, and (d) Ag/ZnO film/RE composite films, respectively.

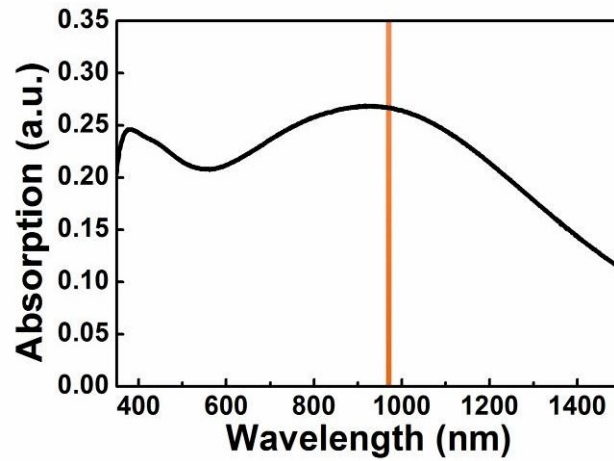


Figure S4. Absorption spectrum of the Ag film. For guidance, the position of incident 980 nm LD is provided.

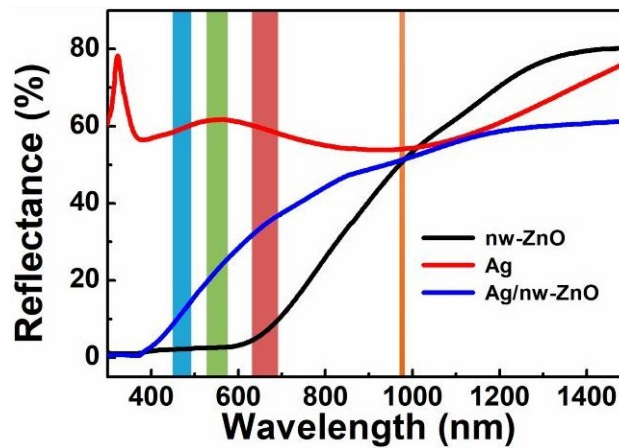


Figure S5. Reflection spectra of the Ag, nw-ZnO, and Ag/nw-ZnO films. For guidance, blue, green, and red emission bands are provided with the position of the incident 980 nm LD.

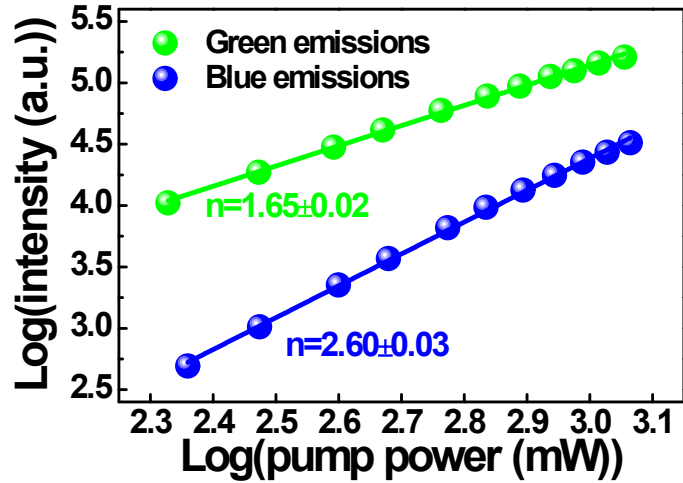


Figure S6. Green and blue UCL intensity versus LD power for the Er^{3+} and Tm^{3+} doped Ag/nw-ZnO/RE composite films.

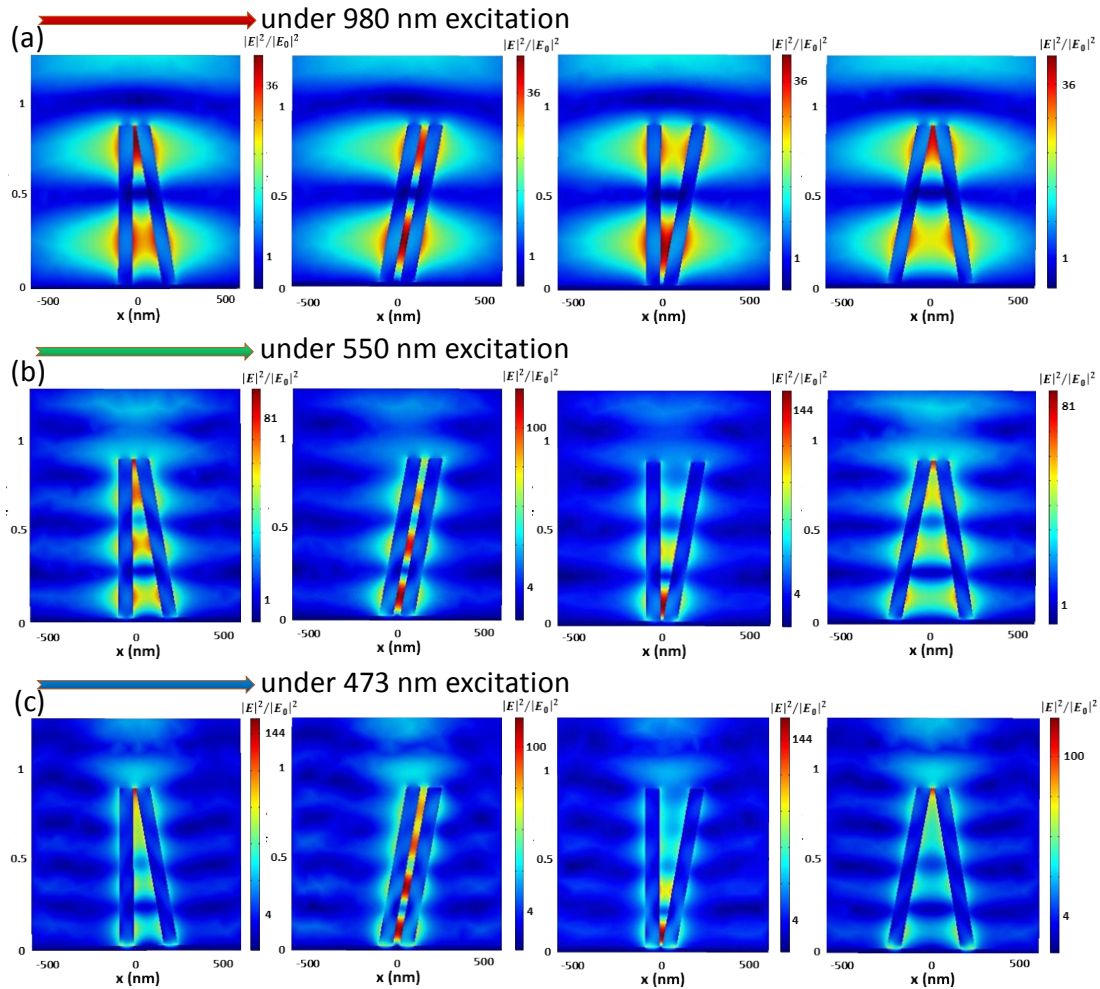


Figure S7. Simulated electric field intensity distribution of different Ag/nw-ZnO spatial gap modes at the wavelength of (a) 980 nm, (b) 550 nm, and (c) 473 nm. The length of the nw-ZnO and thickness of Ag layer are 900 nm and 28 nm, respectively.

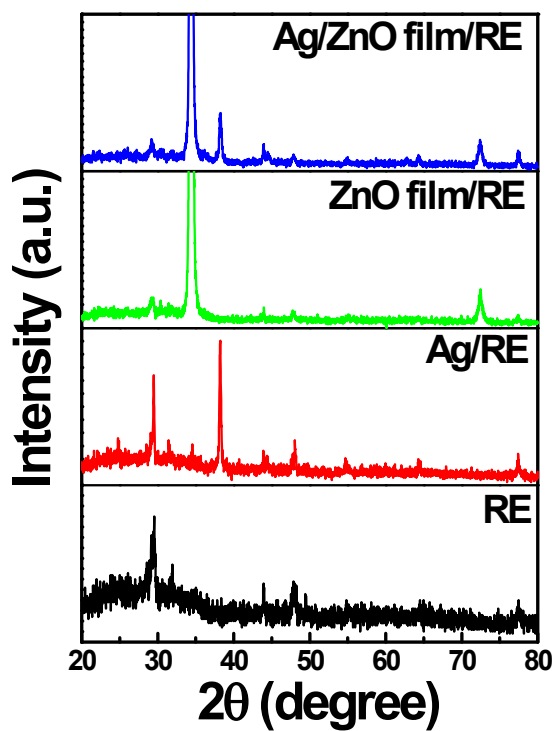


Figure S8. XRD patterns of the RE, Ag/RE, ZnO film/RE, and Ag/ZnO film/RE composite films.

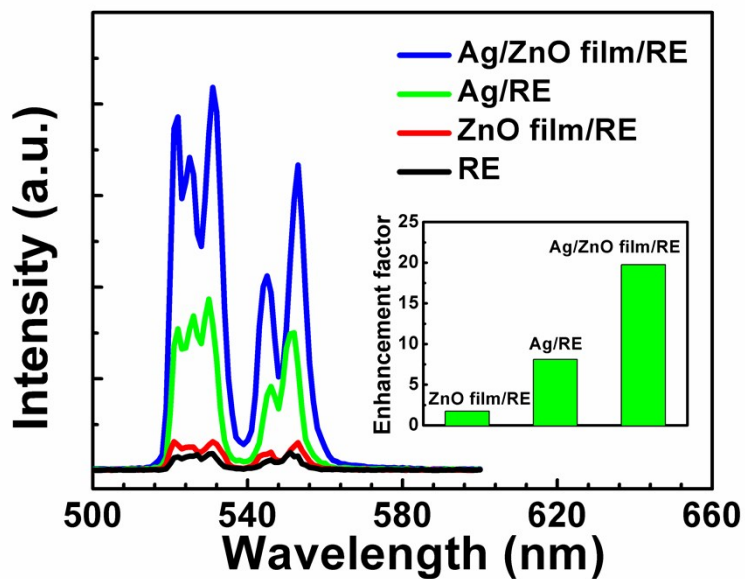


Figure S9. UCL spectra of the RE, ZnO film/RE, Ag/RE, and Ag/ZnO film/RE films. The inset shows the respective enhancement factors of green (Er³⁺) UCL.