Supplementary Information

Enhanced upconversion luminescence on plasmonic architecture of Au-Ag nanocages

Ze Yin, Xinran Zhang, Donglei Zhou, He Wang, Wen Xu, Xu Chen, Tianxiang Zhang, and Hongwei Song

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.

College of Physics, Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.

* Corresponding Authors. E-mail: wen_xu09@163.com; songhw@jlu.edu.cn.
Supplementary Methods

Synthesis of upconversion nanocrystals. NaYF₄:Yb³⁺, Er³⁺ UCNPs were prepared by the well-known solvothermal method.¹ In a typical procedure to synthesis OA-coated NaYF₄:Yb³⁺, Er³⁺ NPs, NaYF₄:20% Yb, 2% Er platelike nanocrystals were synthesized following this protocol: YCl₃ (0.2367 g), YbCl₃ (0.0775 g) and ErCl₃ (0.0077 g) were mixed with OA (6 ml) and ODE (15 ml) in a 100 ml flask and heated to 160 °C, and then cooled down to 30 °C. methanol solution (6 ml) containing NaOH (0.1 g) and NH₄F (0.148 g) were slowly added into the flask and stirred for 30 min. Subsequently, the solution was slowly heated to evaporate methanol, degassed at 120 °C for 30 min, and then heated to 285°C and maintained for 1.5 h under nitrogen atmosphere. The resulting NPs were precipitated by the addition of ethanol, collected by centrifugation at 9,000 rpm for 20 min, washed with absolute ethanol–cyclohexane (1: 1 v/v) several times and re-dispersed in cyclohexane for the following experiments.

Synthesis of Ag nanocubes. In a typical synthesis, 6 mL ethylene glycol was heated under stirring with a Teflon-coated magnetic stirring bar for 1 h in a 24 mL glass vial. While the EG was heated, EG solutions containing AgNO₃ (48 mg/mL) and poly(vinyl pyrrolidone) (PVP, 20 mg/mL) were prepared. A 3 mM solution of Na₂S in EG was also prepared 45 min prior to injection. Shortly after injecting the sulfide solution, 1.5 mL and 0.5 mL of the PVP and AgNO₃ solutions were sequentially injected. Upon injection of the AgNO₃ solution, the reaction mixture went through a series of color changes that included milky white, light yellow, transparent, red, and ocher. The final product -- silver nanocubes -- was obtained by centrifugation and washed with acetone once and ethanol twice to remove EG and excess PVP and finally re-dispersed in deionized water for further use.

Synthesis of Au-Ag nanocages. In a typical synthesis, a fixed amount (0.2 nM; 100 μL) of silver nanocubes was dispersed in 5 mL water containing 1 mg/mL PVP in a 50 mL flask under magnetic stirring and then heated to boil for 10 min. A specific amount of 0.1 mM HAuCl₄ aqueous solution was added to the flask through a syringe pump at a rate of 45 mL/h under magnetic stirring. The solution was heated for another 10 min until the color of the system was stable. Once cooled down to room temperature, the
sample was centrifuged and washed with saturated NaCl solution to remove AgCl and with water several times to remove PVP and NaCl before characterization.

**Fabrication of Au-Ag nanocages nanofilms, NaYF₄/Au-Ag nanocages nanofilms.** Firstly, the square region with the area of 0.5×0.5 cm² on the glass substrate were fabricated by covering two groups of parallel single-layer of adhesive tape (Scotch, 3 M). Then, a drop of the Au-Ag nanocages solution was applied to the center of the square region, followed by drying at room temperature. The Au-Ag nanocages were self-assembled onto the square region of the glass substrate with the evaporation of the liquid. The thickness of Au-Ag nanocages nanofilms were purposively controlled by repeating the above preparation process. Then, the prepared Au-Ag nanocages nanofilms were dropped vertical into the NaYF₄ cyclohexane solution dissolving of NaYF₄:Yb³⁺, Er³⁺ UCNPs and placed in an oven at 35°C for over 4 hours. With the slowly volatilizing of cyclohexane, the NaYF₄:Yb³⁺, Er³⁺ UCNPs were laxly self-organized onto the Au-Ag nanocages or deposited directly on the surface of the glass substrate, driven by capillary force of the liquid in the evaporating process.

**Optical Measurements.** The emission and excitation spectra of all samples were recorded with a SENS-9000 spectrometer. In the measurement of UCL spectra and dynamics of the hybrids films, a photomultiplier combined with a monochromator was used for signal collection from 350 nm to 750 nm. A continuous 980-nm diode laser was used to pump the samples to investigate the steady-state spectra. In the measurements of luminescent dynamics, the samples were pumped using a laser-system consisting of a Nd:YAG pumping laser (1064 nm), a third-order Harmonic-Generator (355 nm) and a tunable optical parameter oscillator(OPO, Continuum Precision II 8000) with a pulse duration of 10 ns, a repetition frequency of 10 Hz and a line width of 4–7 cm⁻¹. Transmittance spectroscopy, and extinction spectroscopy of all samples at every step of the experiments were measured with a UV-1800 UV/visible/NIR spectrophotometer (Shimadzu, Japan), in the 400 and 1100 nm wavelength range.

**Calculation of the nonradiative relaxation rate.** Based on the multi-phonon relaxation theory, the nonradiative relaxation rate with temperature can be written as
\[ W_{NR}(T) = W_{NR}(0)[1 - \exp(-\hbar \omega / kT)]^{-\Delta E / \hbar \omega} \]  

where \( W_{NR}(0) \) presents the nonradiative relaxation rate at absolute zero, \( \hbar \omega \) is the average phonon energy, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature in K, \( \Delta E \) is the energy difference between upper and lower energy levels from which nonradiative relaxation occurs.

In our case, to the two-photon populating \( ^2H_{11/2} \rightarrow ^4S_{3/2} \), the \( \Delta E \), the energy difference between \( ^2H_{11/2} \) and its nearest down level \( ^4S_{3/2} \) is 740 cm\(^{-1}\). When phonon energy \( \hbar \omega \) is in the vicinity of 350 cm\(^{-1}\), the variation of \( W_{NR} \) with the temperature could be carried out.

**Figure S1** EDX spectra of Ag nanocubes, Au-Ag nanocages-3 and Au-Ag nanocages-5.

The EDX spectra of the Ag nanocubes, Au-Ag nanocages-3 and Au-Ag nanocages-5 were compared, as shown in Figure S3. It can be seen that the Au to Ag ratio becomes bigger with the SPR peak red shift (Figure 1f). It suggests that with increasing amounts of HAuCl\(_4\) solution added to the reaction, the dealloying of Ag from the Au-Ag alloyed walls increases, leading to the ratio increasing of Au:Ag in Au-Ag nanocages.
**Figure S2** The cross-section images of the NaYF$_4$: Yb$^{3+}$, Er$^{3+}$/Au-Ag nanocages nanofilm(a), Ag nanocubes nanofilm(b) and NaYF$_4$: Yb$^{3+}$, Er$^{3+}$/Ag nanocages nanofilm(c).

**Figure S3** The transmittance spectra of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ nanofilm, NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Ag nanocubes nanofilm and NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au-Ag nanocages nanofilm.

From the cross-section images, after the deposition of NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs on the Au-Ag nanocages nanofilm, the thickness of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$/Au-Ag nanocages nanofilm hybrid is ~310 nm (Figure S2). The thickness of Ag nanocubes nanofilm is about 200nm. After the deposition of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ NPs, very thin UCNPs films are deposited upon of Ag nanofilm (about 100 nm), which indicates the UCNPs films on glass substrate, Ag nanofilm, and Au-Ag nanocages are nearly the same.

Furthermore, we compared the extinction of NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs on the glass and NaYF$_4$/Ag nanocubes nanofilm and NaYF$_4$/Au-Ag nanocages nanofilm (Figure S3), by using the Eqs. $A_i = \log(1/T_i), i = 1, 2, 3$ (i=1 represents the film on glass, i=2 represents the NaYF$_4$/Ag nanocubes nanofilm and i=3 represents the NaYF$_4$/Au-Ag nanocages nanofilm). It is determined that $A_1=1.27$, $A_2=1.32$ and $A_3=1.29$, which indicates that the relative thickness of the NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs on the Ag nanocubes nanofilm and Au-Ag nanocages nanofilm is close to that on the glass substrate. It should be noted that in the following experiments on the EF of UCL, the influence of the thickness of NaYF$_4$ has been considered.
The intensity ratio of $^2H_{11/2}$ to $^4S_{3/2}$ level for pure NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ film, NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Ag nanocubes nanofilm and NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au-Ag nanocages nanofilm.

The intensity ratio ($R_{HS}$) of $^2H_{11/2} - ^4I_{15/2}$ to $^4S_{3/2} - ^4I_{15/2}$ as a function of excitation power in different samples is characterized. It can be seen that under the same excitation power, NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Ag nanocubes nanofilm and NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au-Ag nanocages nanofilm demonstrate a much higher $R_{HS}$ than the pure NaYF$_4$ film. This means, the coupling of the Ag nanocubes/ or Au-Ag nanocages with NaYF$_4$ induces not only enhanced excitation field, but also strong thermal transmission from metal to NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs.

References