Supporting Information

Dual LSPR of Au/$W_{18}O_{49}$ heterostructures for Upconversion Enhancement and Application of Molecules Detection

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1. Experimental section

Fabrication of $W_{18}O_{49}$ NWs film on F-doped SnO_2 (FTO) glass: The $W_{18}O_{49}$ NWs were prepared through a typical solvothermal approach. 25 mg of $W(CO)_6$ was dissolved into 20 mL of alcohol with stirring for 40 min, then the mixture was transferred into a teflon-lined autoclave. A cleaned FTO glass with size of 2 cm ×3 cm was placed into the autoclaved, and autoclaved was sealed and reacted at 180 °C for 12 h. After reaction, the $W_{18}O_{49}$ NWs film grown on FTO glass with blue color was taken out and washed with ethanol repeatedly.

Preparation of Au NRs: The Au NRs were synthesized through the seed-mediated growth method. [1] First of all, we synthesized the seed solution for Au NRs growth. 5 mL of $HAuCl_4$ solution (0.5 mM) were added into 20 mL scintillation vial, and 5 mL

of CTAB solution (0.2 M) was added as the capping agent. 0.6 mL of freshly prepared 0.01 M of $NaBH_4$ was injected into the Au(III)-CTAB solution under vigorously stirred at 1200 rpm. After the color of the reaction solution discolored from yellow to brownish yellow, the seed solution was stirred for 2 min and was aged for 30 min before further use. After that, the growth solution of Au NRs was gotten as follows: 7.0 g (0.037 M in the final growth solution) of CTAB and 1.234 g (0.047 M in the final growth solution) of NaOL were dissolved in 250 mL ultrapure water at 50 °C. The dissolved solution was proceed to cool down to 30 °C, then 24 mL of $AgNO_3$ solution (4 mM) was added. Undisturbed for 15 min, 250 mL of 1 mM $HAuCl_4$ solution was transfused in the mixed solution. The solution became colorless after stirring (700 rpm) for 90 min, and 2.4 mL of HCl (37 wt. % in water, 12.1 M) was then introduced for adjusting the pH value. Stirring slowly (400 rpm) for 15 min, 1.25 mL of ascorbic acid (AA) was added with stirring vigorously for 30 s. Then 0.8 mL seed solution was injected into the growth solution, which was stirred for 30 s and then was undisturbed at 30°C for 12 h. The resultant solution was centrifuged at 7000 rpm for 30 min. The supernatant is then removed and re-dispersed into 10 mL water.

Synthesis of $NaYF_4$:Yb^{3+},Er^{3+} NPs: The $NaYF_4$ NPs were prepared by a facile pyrolytic reaction. $ErCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$ and $YCl_3 \cdot 6H_2O$ in the molar ratio of 1:10:50 for Er^{3+}:Yb^{3+}:Y^{3+} were dissolved in 6mL oleic acid and 15 mL octadecene solution in a round-bottomed flask containing. After vacuum treatment for 30 min, the mixed solution was kept at 150 ℃ constant temperature for about 20 min until a homogeneous solution was formed, then was cooled down to room temperature.

Simultaneously 4 mmol NH_4F and 2.5 mmol NaOH were dissolved in 10mL methanol, which was then continuously injected into the above solution at a definite rate. The solution was heated to evaporate methanol at 80 ℃ for 1.5 h, and followed by further heating to 305 ℃ for 1.5 h under a nitrogen atmosphere. The products were cooked and washed by cyclohexane/ethanol liquid with a volume ratio of 1:3, and finally re-dispersed in cyclohexane.

Fabrication of $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs film: The composite films were self-assembled by the solvent evaporation method. The prepared $W_{18}O_{49}$ NWs film was immersed into Au NRs aqueous solution and placed in an oven at 50 °C for 6 h. With the slowly volatilizing of aqueous solution, Au NRs were assembled on the $W_{18}O_{49}$ NWs film through the surface tension of the solution during evaporation. Then $NaYF_4$ NPs were dissolved in cyclohexane solution and further assembled on the above obtained Au NRs/$W_{18}O_{49}$ NWs film, as mentioned above.

Fabrication of reference samples: the reference sample $NaYF_4/W_{18}O_{49}$ was self-assembled by the solvent evaporation method which was similar to fabrication of the $NaYF_4/Au/W_{18}O_{49}$. And the reference sample $NaYF_4$ and $NaYF_4$/Au were fabricated on the non-plasmonic $W_{18}O_{49}$ film treated by H_2O_2 to passivate the surface oxygen vacancies, which is to quench the LSPR absorption feature of $W_{18}O_{49}$ and make identical structural features and component morphology with the $NaYF_4/Au/W_{18}O_{49}$ hybrids sample.

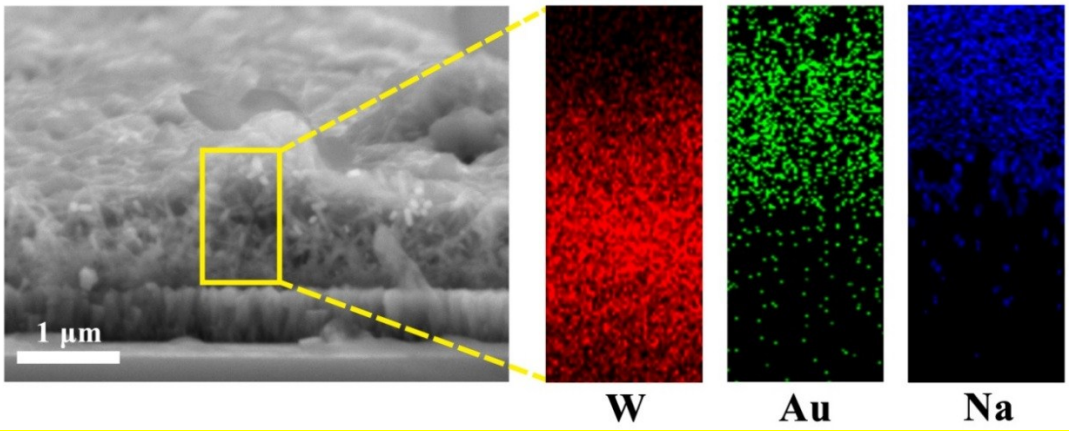
2. Characterization

The morphology, elemental component analysis and structures of samples were checked out on the Scanning Electron MicroscopyXL-30 ESEM FEG(SEM) with energy dispersive spectrometer (EDS), transmission electron microscopy JEOL JEM-

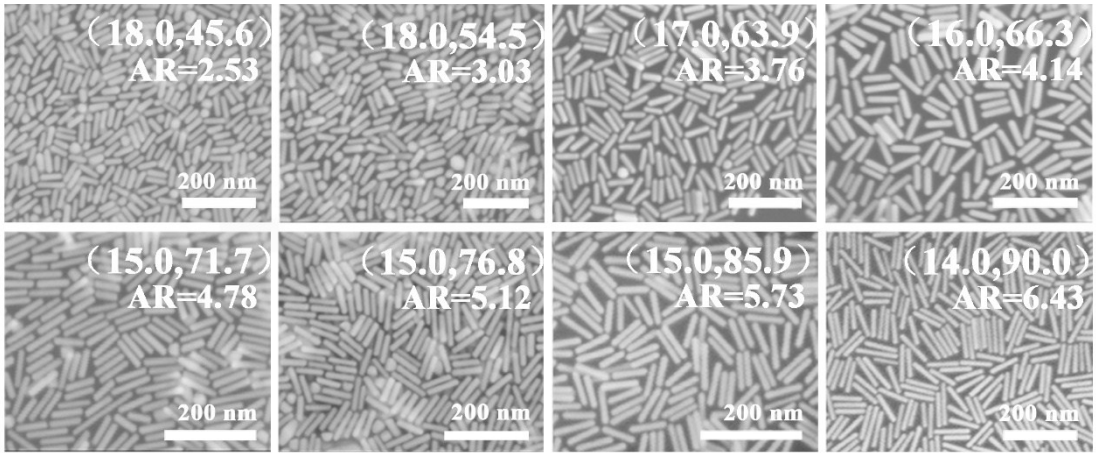
2100(TEM) . The Lambda 750 UV-vis-NIR spectrophotometer was used to analyze the extinction properties of samples. The UCL spectra were measured by a collected with an inverted microscope Olympus IX71combined with a Jobin Yvon iHR550 monochromator. The Surface Enhanced Raman Scattering (SERS) properties of samples were carried out on a Renishaw in Via Raman microscope.

Three-Dimensional Finite-Difference Time-Domain Simulation: 3D-FDTD calculations were performed by use of a commercial FDTD software package (Lumerical Solutions) for investigate the electric field enhancement induced by LSPR of plasmonic nanoparticles ($W_{18}O_{49}$ NWs, Au NRs and Au NRs/$W_{18}O_{49}$ NWs). In this calculation, to appropriate the experimental condition, the Au NRs/$W_{18}O_{49}$ NWs heterostructures system was simplified as three of $W_{18}O_{49}$ nanowire (diameter D_1 = 10 nm) and an Au nanorod (Length L_1 = 75 nm, diameter D_2= 15 nm). An incident light was propagated from the Y direction and polarized along the Z direction. The wavelength was set to be 980, 522, 540 and 654 nm, respectively. To account for small morphological details and ensure good numerical convergence, the override mesh cell size used was $1\times1\times1$ nm^3.

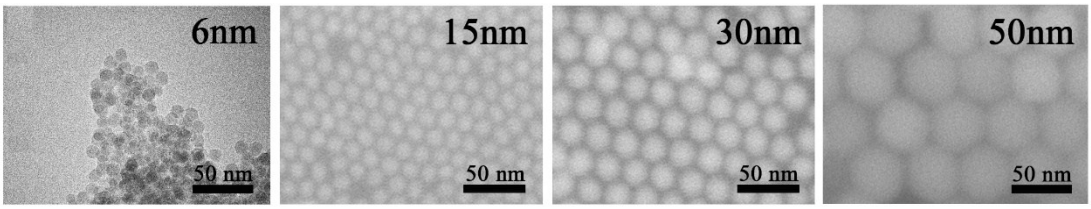
3. Supplementary Figures



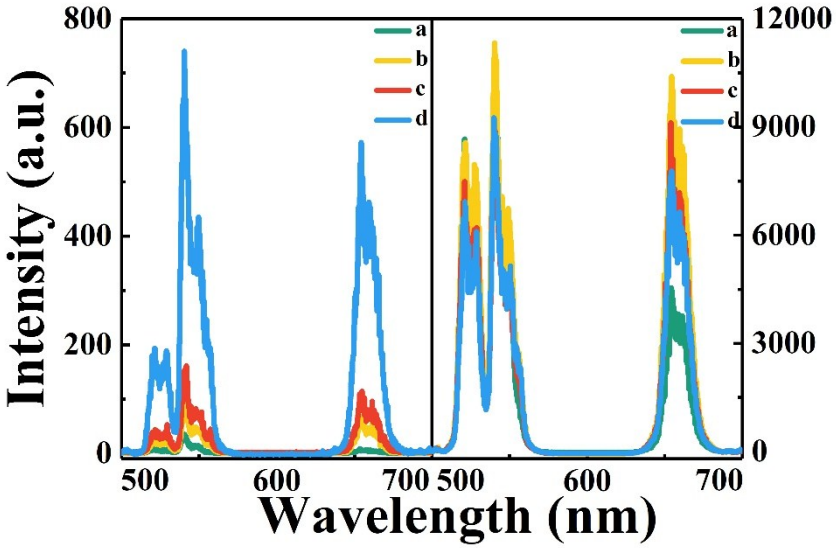
S1. SEM image and the corresponding elemental mapping images of cross-section of $NaYF_4$/Au/$W_{18}O_{49}$ composite film.



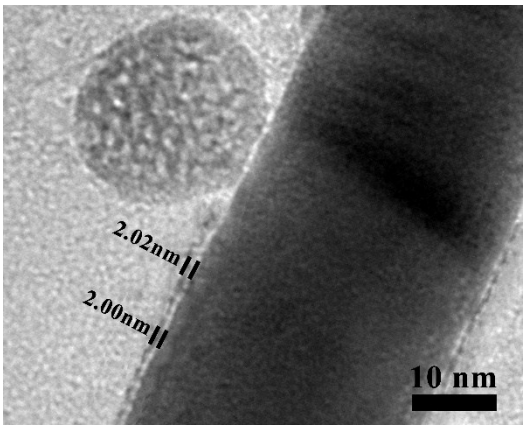
S2. SEM image of Au NRs with increasing aspect ratio.



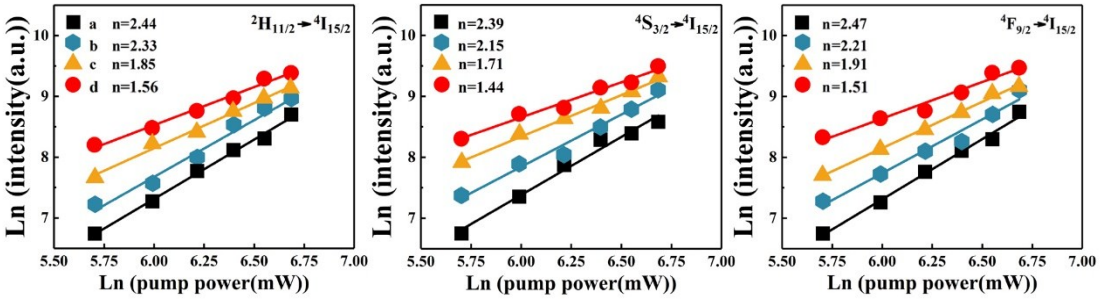
S3. The SEM image of different gain sizes of $NaYF_4$ NPs.



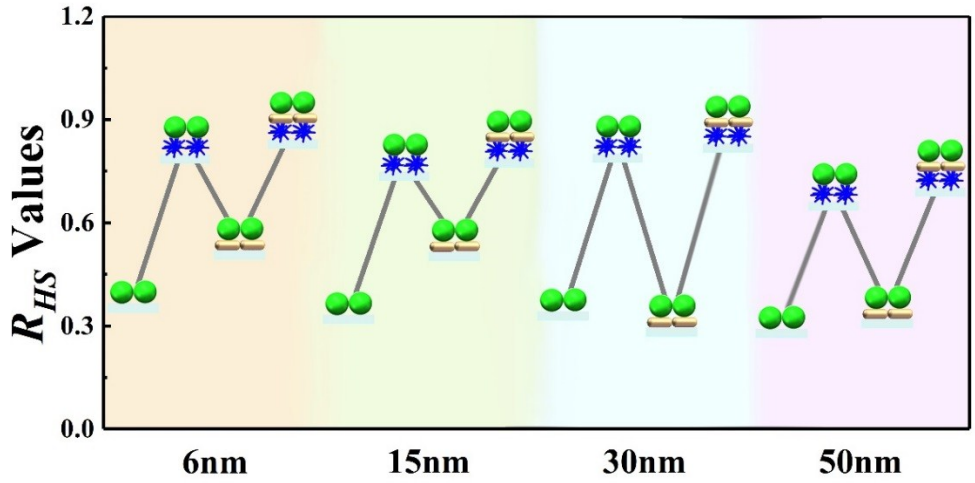
S4. UC emission spectra of left: a) 6 nm $NaYF_4$ NPs, b) 15 nm $NaYF_4$ NPs, c) 30 nm $NaYF_4$ NPs, d) 50 nm $NaYF_4$ NPs; right: a) 6 nm $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs, b) 15 nm $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs, c) 30 nm $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs, d) 50 nm $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs hybrid film.



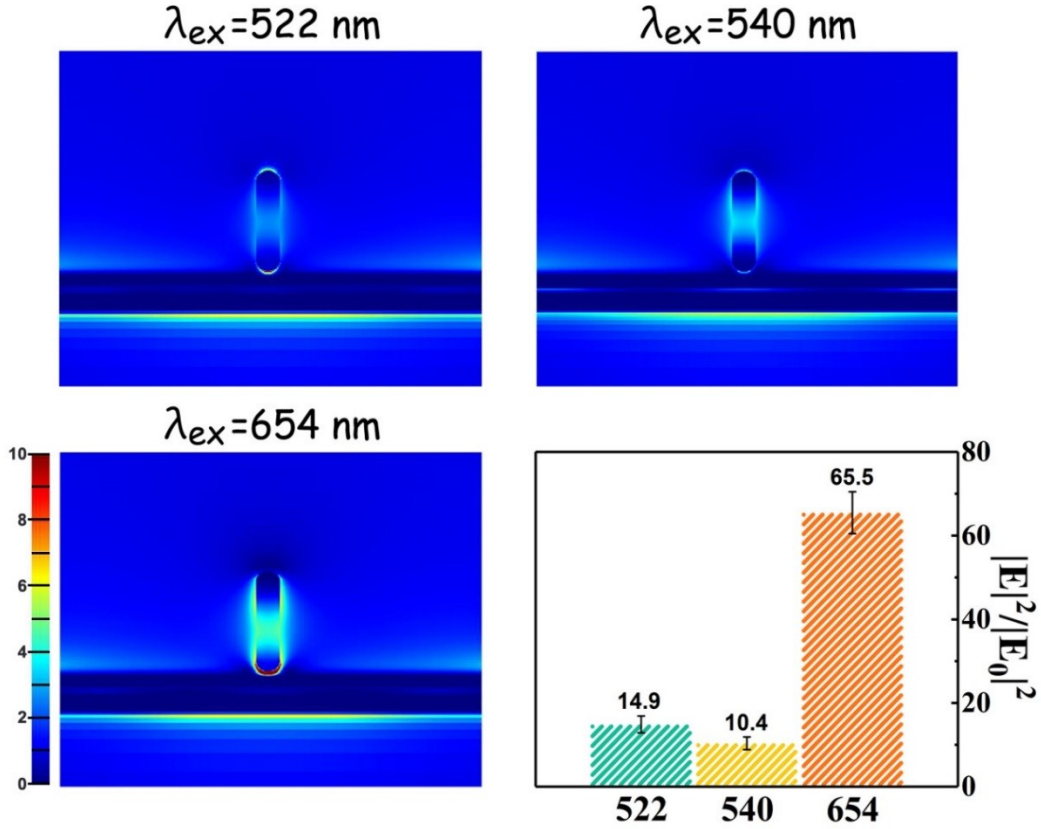
S5. The TEM image of $NaYF_4$/Au/$W_{18}O_4$ hybrid film treated by PVP solution with the best thickness (2 nm).



S6. Power density dependent UCL intensity of $^2H_{11/2}$-$^4I_{15/2}$, $^4S_{3/2}$-$^4I_{15/2}$, and $^4F_{9/2}$-$^4I_{15/2}$ transitions under 980 nm irritation for a) $NaYF_4$ NPs, b) $NaYF_4$ NPs/$W_{18}O_{49}$ NWs, c) $NaYF_4$ NPs/Au NRs, d) $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs hybrid film.



S7. R_{HS} values as a function of different grain size of $NaYF_4$ NPs in the $NaYF_4$ NPs, $NaYF_4$ NPs/$W_{18}O_{49}$ NWs, $NaYF_4$ NPs/Au NRs, $NaYF_4$ NPs/Au NRs/$W_{18}O_{49}$ NWs hybrid film.



S8. Electric field distributions of simulation model of Au NRs/$W_{18}O_{49}$ NWs (vertical contact model) under different light excitation.

REFERENCES

(1) Ye, X.; Zheng, C.; Chen, J.; Gao, Y.; Murray, C. B. Using binary surfactant mixtures to simultaneously improve the dimensional tunability and monodispersity in the seeded growth of gold nanorods. *Nano Lett.* **2013,** 13, 765-771.