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# NIR LSPR-coupling of Ag nanorices and $W_{18}O_{49}$ nanowires: Application of LRET and SERS

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## ABSTRACT

Broadband plasmonic nanomaterials working in the near-infrared (NIR) region which can concentrate and transfer the low-energy NIR light in the upconversion system are desired. However, single plasmon regulation often fails to meet requirement. Herein, a new type of  $Ag/W_{18}O_{49}$  binary composite film composed of a metal domain (Ag nanorices) and a semiconductor domain ( $W_{18}O_{49}$  nanowires) is designed and fabricated, which exhibits a broad and strong localized surface plasmon resonance (LSPR) across visible to NIR wavelengths, arising from interactions between the two nanostructure domains. The experimental and theoretical studies demonstrate that the localized electric field is dramatically amplified due to an NIR-driven strong plasmonic coupling of LSPR. In particular, the resonance excitation of plasmonic coupling in the  $Ag/W_{18}O_{49}$  composite film induces remarkable enhancement of upconversion via the LSPR effect, and simultaneously provides ultrasensitive surface-enhanced Raman scattering (SERS) by the enhanced electromagnetic field. This work demonstrates a new strategy for accurate molecular detection by assembling upconversion nanoparticles (UCNPs) on  $Ag/W_{18}O_{49}$  composite film, and the so-formed NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> multilayer film can support both the quantitative detection by luminescence resonance energy transfer (LRET) and the qualitative detection by SERS.

## 1. Introduction

Rare-earth doped upconversion nanoparticles (UCNPs) with the unique optical properties and broad application have attracted much attention [1–3]. It can convert near-infrared (NIR) incident light into short wavelength ultraviolet or visible emissions, making these UCNPs useful supplementary photovoltaic materials [4–6], such as the well-known trivalent lanthanide ions ( $Ln^{3+}$ ) doped NaYF<sub>4</sub> nanoparticles [7,8]. The sweeping applications of UCNPs in biological imaging, solar cell, fluorescent probe and other fields have made researchers realize the significance of improving upconversion luminescence (UCL) efficiency [9–12]. Among all the attempts to solve this problem, localized electric filed enhancement by surface plasmon has been employed to be an effective method to improve UCL efficiency [13,14]. As a classic optical antenna, noble metal nanostructures with tunable localized surface plasmon resonance (LSPR) energy depended on shape and size are frequently introduced into UCNPs to effectively increase UC emission

intensity via localized electric field amplification [15,16]. However, the light trapping ability of most current noble metals is confined to very limited visible region and within a narrow range [17–19], therefore, broadband plasmonic nanomaterials working in the NIR region are desired. More recent studies were based on overcoming this issue, for example, Lin has utilized gold dendritic nanoforests deposited on titanium nitride/silicon wafers composite substrate to achieve wide absorbance band ranging from 350 to 900 nm [20]. Xiong recently developed a flexible NIR photovoltaic device by coupling Si nanowires with an Ag-nanoplate-based plasmonic antenna which possesses a surface plasmon extinction band ranging from 550 to 1100 nm [21]. Song reported an Ag NW-net plasmonic antenna exhibits super wide surface plasmon extinction from 350 to 3000 nm [22]. But manipulating the shapes and sizes of these specific metallic structures requires a very complex synthesis process, and using noble metals inevitably suffers from high cost.

Recently, the low cost heavily doped semiconductor plasmonic nanostructures, such as  $Cu_{2,x}S$ , Sn-doped  $In_2O_3$ ,  $WO_{3-x}$ , and  $MOO_{3-x}$ ,

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Received 11 August 2020; Received in revised form 15 October 2020; Accepted 9 November 2020 Available online 22 December 2020 0925-4005/© 2020 Published by Elsevier B.V. have also been investigated to focus incident light and substantially improve the surrounding electric field through the "optical antenna". Adjusting stoichiometric ratios, vacancy and phase structures, the LSPR band and intensity of semiconductor can be easily regulated, thus can match simultaneously the excitation and emission bands of lanthanidedoped UCNPs [23-26]. LSPR-induced luminescence enhancement based on various noble metal and semiconductor nanostructures has been investigated and applied in optoelectronic, photocatalysis, and photovoltaic devices [27,28]. Nevertheless, the challenge of effectively improving the UCNPs efficiency has been a bottleneck in various single plasmonic mode of noble metal or semiconductor nanostructures. In a plasmonic point of view, the LSPR-coupling effect between two or more noble metal nanostructures can greatly enhance the localized electromagnetic field [29–31]. With the excessive development of plasmonic semiconductors, inexpensive heavily doped semiconductor nanostructures have been considered as potential choice to be coupled with noble metal nanostructures [32]. The optical properties of the binary structures simultaneously display both of LSPR characteristics in the metal-semiconductor system, which is substantially different from the sum of their components. Combination of plasmonic metal with semiconductor nanostructures is substantially different from the methods generally used for tailoring LSPR by controlling the size and the shape of metal nanostructures which have often been used to create strong wide absorbance [33,34].

In this work, we develop a novel type of plasmonic coupling Ag nanorices/W18O49 nanowires (Ag NRs/W18O49 NWs) composite film. And the utilization of double plasmonic mode generated from Ag NRs and W<sub>18</sub>O<sub>49</sub> NWs as optical antennas to enhance the UCL of NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs  $(Ln^{3+}=Yb^{3+}-Tm^{3+}, Yb^{3+}-Er^{3+})$  are investigated. The hybridization of Ag NRs and W18O49 NWs synergistically amplify the electric field environment around UCNPs, which breaks through the boundedness of single LSPR and further elevate the UCL enormously. Note that surfaceenhanced Raman scattering (SERS) in the noble metal and semiconductor nanostructures is an ultrasensitive vibrational spectroscopic technique. A key design characteristic of the NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> composite film is to obtain the SERS and luminescence resonance energy transfer (LRET) in one single composite film simultaneously. Using this unique feature, we develop a novel dual purpose sensor, in which achieves from qualitative to quantitative detection with high sensitivity by using the SERS signal monitoring and fluorescence sensing.

#### 2. Materials and methods

## 2.1. Preparation of Ag NRs

The Ag NRs were prepared in a facile polyol reduction [35]. To an aqueous polyvinyl pyrrolidone (PVP, 2 mL, 1 M, Mw $\approx$ 40 000) solution in Polyethylene glycol 600 (PEG 600, 10 mL) was added AgNO<sub>3</sub> (0.2 mL, 1 M) under slow stirring. The round-bottomed bottle is placed in an oil

bath and heated at 100  $^{\circ}$ C for 8 h, resulting in a color change from transparent to gray-green. The final solution was washed four times with acetone or ethanol and collected (Fig. 1a).

## 2.2. Synthesis of NaYF<sub>4</sub> UCNPs

NaYF<sub>4</sub>: 20 % Yb<sup>3+</sup>,0.5 % Tm<sup>3+</sup> (or 20 % Yb<sup>3+</sup>, 2% Er<sup>3+</sup>) NPs were synthesized following this typical pyrolytic process [36]: 1 mmol RECl<sub>3</sub>·6H<sub>2</sub>O (RE = Y, Yb, Tm, Er) were proportionally poured into the flask with 6 mL oleic acid and 15 mL octadecene. Vacuuming for 30 min, then the mixture solution was heated to 150 °C for dissolving the rare earth. It was cooled to room temperature after 20 min. After that, the solution that NH<sub>4</sub>F (4 mmol) and NaOH (2.5 mmol) were dissolved in 10 mL methanol was continuously added to the flask. In order to fully exclude methanol, the temperature was raised to 80 °C for 1.5 h. The final product was obtained by heating to 305 °C for 1.5 h and then cooling. At last, the product in cyclohexane/ethanol liquid with a volume ratio of 1:3 was centrifugally washed three times and dispersed in cyclohexane (Fig. 1b).

### 2.3. Fabrication of W<sub>18</sub>O<sub>49</sub> NWs

The W<sub>18</sub>O<sub>49</sub> NWs were synthesized by solvothermal process. W(CO)<sub>6</sub> (25 mg) was added to alcohol (20 mL) and stirred for 40 min. Then the reactants were transferred into a stainless steel reaction vessel containing  $2 \times 3$  cm F-doped SnO<sub>2</sub> (FTO) glass and sealed for 12 h at 180 °C. Finally, the FTO was removed from the autoclave and washed with ethanol.

## 2.4. Fabrication of NaYF<sub>4</sub>/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film

With slow solvent evaporation, a certain concentration of Ag NRs was self-assembled onto  $W_{18}O_{49}$  NWs film. NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs were deposited on Ag NRs/ $W_{18}O_{49}$  NWs layer on account of similar preparation approach. Based on a similar fabrication progress, three other control films were also prepared: NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs were self-assembled on  $W_{18}O_{49}$  NWs film; NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs were self-assembled on N- $W_{18}O_{49}$  NWs film treated by H<sub>2</sub>O<sub>2</sub> to quench the LSPR characteristic, the obtained NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/N- $W_{18}O_{49}$  NWs film was abbreviate to NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs were self-assembled on N- $W_{18}O_{49}$  NWs film, then NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs were deposited on Ag NRs/N- $W_{18}O_{49}$  NWs, the obtained NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/N- $W_{18}O_{49}$  NWs film, was abbreviate to NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/N- $W_{18}O_{49}$  NWs film was abbreviate to NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs film.

#### 2.5. Characterization

The Lambda 750 UV–vis-NIR spectrophotometer was used to analyze the extinction properties of samples. The UCL spectrum was measured by a collected with an inverted microscope Olympus IX71 combined



Fig. 1. SEM images of a) Ag NRs and b) NaYF<sub>4</sub> NPs.

with a Jobin Yvon iHR 550 monochromator. The morphology, elemental component analysis and structures of samples were checked out on the Scanning Electron Microscopy XL-30 ESEM FEG (SEM) with energy dispersive spectrometer (EDS) and transmission electron microscopy JEOL JEM-2100 (TEM). The Surface Enhanced Raman Scattering (SERS) properties of samples were carried out on a Renishaw in Via Raman microscope.

#### 2.6. Theoretical calculation

We performed theoretical calculations for all sample models by three-Dimensional Finite element method (FEM) simulation. The simulated sample models are located in a homogeneous medium with a refractive index of 1. W<sub>18</sub>O<sub>49</sub> NWs (diameter D<sub>1</sub> = 10 nm) bundle (three wires merging together), Ag NRs (diameter D<sub>2</sub> = 450 nm, D<sub>3</sub> = 50 nm) and W<sub>18</sub>O<sub>49</sub> NWs/Ag NRs are calculated at different contact positions under the stimulation of 980 excitation light. Objects are formatted using non-uniform, the maximum of which are install to be less than  $\lambda/6$ . Scattering of the external boundary needs to be minimized with a perfect matching layer (PML). Placing a simulated sample model on the X-Z plane, the incident light polarizes at 1 V/m in the Z direction and propagates in the Y direction.

## 3. Results and discussion

A simple method for preparing NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film is realized in a specific order. More specifically, a fabrication process consists of a series of steps are executed sequentially or partially in parallel as shown in Fig. 2: (1) Ag NRs with the average diameters of ~50 nm and lengths of ~450 nm (Fig. 1a) are fabricated by an ingenious polyol reduction [35]; (2) The NaYF<sub>4</sub> NPs with single-dispersed and homogeneous nanostructure are prepared by a facile pyrolytic reaction according to the previously reported (Fig. 1b) [36]; (3) W<sub>18</sub>O<sub>49</sub> NWs grows on FTO glass substrate via solvothermal technique, which are able to keep free-standing without stacking or agglomeration (as shown in Fig. 3a and d). The SEM shows that the W18O49 NWs substrate is particularly favorable for easy loading of the Ag NRs and NaYF4 NPs in the next steps; (4) The Ag NRs are densely distributed and intercalated into the W<sub>18</sub>O<sub>49</sub> NWs forming the Ag/W<sub>18</sub>O<sub>49</sub> composite film (see the Fig. 3b and e) through a solvent evaporation method. Furthermore, the randomly tilted growth of W<sub>18</sub>O<sub>49</sub> NWs on the film enable the majority of deposited Ag NRs to directly contact the side surface of the W18O49 NWs, which is helpful to form interactions between the two domains in the plasmonic-coupling  $Ag/W_{18}O_{49}$  composite film; (5) After the deposition of NaYF4 NPs by the similar fabrication method, a thin UC luminescence layer is formed above the plasmonic layer, the profile of NaYF<sub>4</sub> NPs can be clearly distinguished from the top view of SEM image of the NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> film (Fig. 3c). The cross-section SEM image in Fig. 3f shows that the NaYF4 NPs are interconnected and covered the top surface of the Ag/W<sub>18</sub>O<sub>49</sub> plasmonic film, thus confirming the formation of the NaYF<sub>4</sub> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs layer structured composite film.

XRD pattern shows that the concomitance of four characteristic diffraction peaks, namely cubic phase of Ag, monoclinic of  $W_{18}O_{49}$ , hexagonal phase of NaYF<sub>4</sub>, in the NaYF<sub>4</sub> NPs/Ag NRs/ $W_{18}O_{49}$  NWs hybrid film, and the tetragonal phase of SnO<sub>2</sub> is ascribed to FTO glass substrate (Fig. 3g). The EDS pattern (Fig. 3h) further confirms the identity and content of the NaYF<sub>4</sub>/Ag/ $W_{18}O_{49}$  hybrid in which O, W, Na, F, Y, and Ag co-existed. LSPR characteristic can be acquired by comparing the surface plasmon extinction of the Ag/ $W_{18}O_{49}$  hybrid film with individual Ag NRs and  $W_{18}O_{49}$  NWs films. (Fig. 3i). Ag NRs film displays two types LSPR behaviors that are intrinsic absorption of transverse mode at 1450 nm (the green curve). A broad plasmonic extinction range of  $W_{18}O_{49}$  NWs film extends beyond the visible to NIR regions (the blue curve), which derives from a large number of highly mobile electrons due to the abundant oxygen vacancies. The optical features of the



Fig. 2. Schematic diagram of the fabrication process of NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs, NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs, NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/W<sub>18</sub>O<sub>49</sub> NWs, and NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs films.



**Fig. 3.** The top views and side views of SEM images of  $W_{18}O_{49}$  NWs (a and d), Ag NRs/ $W_{18}O_{49}$  NWs (b and e), and NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/ $W_{18}O_{49}$  NWs (c and f) films. (g) The XRD and (h) EDS pattern of as-fabricated NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs/Ag NRs/ $W_{18}O_{49}$  NWs film. (i) The extinction spectra of as-fabricated films: (1) Ag NRs (green curve), (2)  $W_{18}O_{49}$  NWs (blue curve), and (3) Ag NRs/ $W_{18}O_{49}$  NWs (red curve).

two plasmonic films observed above are basically consistent with the reported Ag NRs and  $W_{18}O_{49}$  NWs nanomaterials, confirming that the extinction capabilities of the nanostructured samples retain invariably after constructing on FTO. It is impressively found that the hybrid Ag/ $W_{18}O_{49}$  film (the red curve) possess simultaneously the two types of extinction spectra characteristics of the individual sample Ag NRs and  $W_{18}O_{49}$  NWs. Meanwhile the extinction band is drastically enhanced in the NIR region which is presumably because of LSPR coupling between Ag NRs and  $W_{18}O_{49}$  NWs.

In the plasmonic point of view, the LSPR coupling effect depends strongly on the shape, sizes, and positions of the plasmonic components of the coupled-nanostructure system [37]. To deeply comprehend how the LSPR coupling enhances the localized electric field in the Ag/W18O49 composite film, simulations of the localized electric field distribution surrounding plasmon Ag/W18O49 under 980 nm excitation via FEM simulation are performed in Fig. 4. In order to show the actual situation in Ag/W18O49 film, relative position of two domains is deliberately shown in the figure, where plasmonic components are geometrically ascribed to three contact types between Ag NRs and x-axis of W18O49 NWs, namely parallel, 45°, and 90° contact models (further divided into tip and cross contact types with a certain angle). Fig. 4 gives the simulations of the electric field distribution surrounding isolated W18O49 NWs and single Ag NRs firstly. The isolated  $W_{18}O_{49}$  NWs are simplified as three nanowires in a bundle model, and the maximum localized electric field intensity enhancement  $(|E|^2/|E_0|^2)$  achieves 4.94 at the plasmonic "hot spots". For the individual Ag NRs, the electric field direction dependence of the localized electric field distributions are observed. The  $|E|^2/|E_0|^2$  value is 8.31 under the transverse electric field direction, reaches 353 for the longitudinal direction. After placing random Ag NRs on the W18O49 NWs, all simplified models achieve remarkable enhancement of the localized electric fields. The  $|E|^2/|E_0|^2$ is about 190-257 which depends on upper-and-lower or side-by-side arrangement models when Ag NRs are arranged in parallel to the x-axis of W18O49 NWs. Comparing the electric field intensity distribution in 45° and 90° contact types, it can be drawn that the increase of  $|E|^2/|$  $E_0|^2$  in the 90° contact model is much more effective than that in parallel or 45° contact models. The enhancement factor in the tip contact type exceeds the values obtained in the cross contact type with the certain angle of  $45^{\circ}$  or  $90^{\circ}$ . When the tip of the Ag NR touches the side surface of  $W_{18}O_{49}$  NW vertically, a maximum enhancement of  $|E|^2/|E_0|^2$  reaches 2080 at the corresponding "hot spot" of Ag/W18O49 interface. The simulations results confirm that the LSPR-coupling of the Ag/W18O49 strongly aggregate and amplify the incident NIR intensity over the separated Ag NRs or W18O49 NWs.

As the "optical antenna", the Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs plasmonic composite film with dual LSPR can amplify the strength of the localized electric field (E), and then resonantly transfer the energy to UCNPs. The UCNPs consequently experience a far more intense excitation electric field based on the surface enhancement effect (shown in Fig. 5a). The strength of UCL could be improved up to  $E^{2n}$  times considering an nphoton nonlinear UCL process [38]. The NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs act as a model emitter to approach the plasmonic nanostructure in the sensitized-UCL investigation. As can be seen from the schematic of UC population and emission processes of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs under 980



Fig. 4. Electric field distributions of the isolated  $W_{18}O_{49}$  NWs, single Ag NRs, and Ag NRs/ $W_{18}O_{49}$  NWs at different contact positive between Ag NRs and x-axis of  $W_{18}O_{49}$  NWs with incident irradiation (980 nm) along the z-axis.

nm laser excitation, the populations on  ${}^{1}D_{2}$  and  ${}^{1}G_{4}$  originate from a four-photon process and a three-photon process, respectively. The dominant blue emission consists of a strong emission at 477 nm corresponding to the  ${}^{1}G_{4}$ - ${}^{3}H_{6}$  transition and a considerable weak emission at 450 nm corresponding to the  ${}^{1}D_{2}$ - ${}^{3}F_{4}$  transition. The weak red emission at 646 nm is attributed to  ${}^{1}G_{4}{}^{-3}F_{4}$  transition (Fig. 5a and b). We sequentially present the luminescence curves of the comparative experiments in the existence of different LSPR effects (Ag NRs, W18O49 NWs, and Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs films) in the regular spectra of NaYF<sub>4</sub>:  $Yb^{3+}$ ,  $Tm^{3+}$  NPs with average size of 10 nm. It is clear that NaYF<sub>4</sub>: $Yb^{3+}$ , Tm<sup>3+</sup> NPs have an obvious breakthrough in UCL intensity approaching the plasmonic nanostructures via plasmonic energy transfer as shown in Fig. 5b. It is further depicted the variation of the enhancement factors for the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> coupled with different plasmonic films in the Fig. 5c. It indicates that the plasmonic effect is more outstanding under the synergy of the dual LSPR from Ag NRs/ $W_{18}O_{49}$  NWs film, rather than the single LSPR effect of Ag NRs or  $W_{18}O_{49}$  NWs. For the case of 10 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub>, the overall UCL intensity increases 295 times, originating from 359 times in  ${}^1\text{D}_2\text{-}{}^3\text{F}_4$  transition, 371 times in  $^1\text{G}_4\text{-}^3\text{H}_6$  transition, and 216 times in  $^1\text{G}_4\text{-}^3\text{F}_4$  transition, as shown in Fig. 5c. The NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs selected to deposit on the plasmonic substrates in this UCL experiment are 10 nm in size, because the effective interaction distance for the LSPR-enhanced near-field effect is limited (less than 10 nm) [39]. As increasing the sizes of NaYF<sub>4</sub>:Yb<sup>3+</sup>,  $Tm^{3+}$  NPs in the NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> film, the enhancement factor of UCL reduces dramatically (Fig. 5d).

The UCL spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs with different sizes under 980 nm excitation are explored in further experiments, as shown in Fig. 6. It is worth noting that the  ${}^{1}D_{2}$ - ${}^{3}F_{4}$  blue emission at 450 nm, which is too weak to be observed in 10 nm NaYF<sub>4</sub>, markedly elevates as the size of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs increases above 15 nm. In contrast to the 10 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs, the intensity ratio of  ${}^{1}D_{2}$ - ${}^{3}F_{4}$  to  ${}^{1}G_{4}$ - ${}^{3}H_{6}$  in 15 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs increases notably from 0.12 to 0.72. As the size gradually increase to be 50 nm, the ratio value of  ${}^{1}D_{2}$ - ${}^{3}F_{4}/{}^{1}G_{4}$ - ${}^{3}H_{6}$  further boosts to be 0.93. Thus, the blue emission in NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs increases from the extending emission region and enhancing emission intensity with the particle size increasing, and the improved ratio of  ${}^{1}D_{2}$ - ${}^{3}F_{4}/{}^{1}G_{4}$ - ${}^{3}H_{6}$  implies the alteration of population channels in the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs. The previous study results indicate that the populating process strongly depends on particle size [40,41]. In the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup> system, the following cross relaxation process may happen [42], as marked in Fig. 5a:

$$Tm(A)^{1}G_{4} + Tm(B)^{3}H_{6} \rightarrow Tm(A)^{3}F_{2,3} + Tm(B)^{3}F_{4}$$
 (1)

$$Tm(A)^{3}F_{3} + Tm(B)^{3}F_{3} \rightarrow Tm(A)^{1}D_{2} + Tm(B)^{3}H_{6}$$
 (2)

Due to the fact that the energy separation between  ${}^{3}F_{2}$  and  ${}^{3}F_{3}$  states is only about 500 cm<sup>-1</sup>, the population distribution between the two states is dominated by thermal distribution. The nonradiative relaxation from  ${}^{3}F_{2}$  to  ${}^{3}F_{3}$  states decrease considerably in smaller nanoparticles, thus the population of  ${}^{3}F_{3}$  decreases. The cross relaxation process in Eq. (2) is therefor not effective, resulting in the depopulation on  ${}^{1}D_{2}$  and a



**Fig. 5.** a) Schematic diagram of the interaction between the double LSPR effect of Ag NRs  $/W_{18}O_{49}$  NWs, and upconversion transition process of the adjacent NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs. b) Upconversion emission spectra of (1) 10 nm NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs, 10 nm NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs coupled with (2) Ag NRs, (3)  $W_{18}O_{49}$  NWs, and (4) Ag NRs/ $W_{18}O_{49}$  NWs under irradiation of 980 nm light, respectively. c) Histogram of enhancement factors of the NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs deposited on the different substrates at different emission wavelengths: (1) Ag NRs, (2) $W_{18}O_{49}$  NWs, (3) Ag NRs/ $W_{18}O_{49}$  NWs. d) UCL enhancement factors of different emission wavelengths as a function of grain sizes for NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs coupled with Ag/ $W_{18}O_{49}$  film.



Fig. 6. Upconversion emission spectra of a) the different sizes of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs, and b) different sizes of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs coupled with Ag NRs/ $W_{18}O_{49}$  NWs film. Insets show the corresponding achieved micro-area optical images under irradiation of 980 nm.

weak emission from  ${}^{1}D_{2}{}^{-3}F_{4}$  transition. More effective cross relaxation process in Eq. (2) happens as the particle size increasing, which accordingly leads to increased intensity ratio of  ${}^{1}D_{2}{}^{-3}F_{4}$  to  ${}^{1}G_{4}{}^{-3}H_{6}$ . The UCL spectra of different size of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs coupled with Ag/ W<sub>18</sub>O<sub>49</sub> plasmonic composite film are shown in Fig. 6b. Great enhancement of the blue emission is obtained by dual LSPR coupling with Ag NRs/ W<sub>18</sub>O<sub>49</sub> NWs, and the enhancement factor of  ${}^{1}D_{2}{}^{-3}F_{4}$ transition is higher than that of  ${}^{1}G_{4}{}^{-3}H_{6}$  transition in the samples bigger than 15 nm (Figs. 5d and 6b). A bright blue emission becomes noticeable on the micro-area photogragh of the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> film (see inset of Fig. 6b). Although 10 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs exhibit optimal enhancement factor in our study, 15 nm NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs show the largest UCL intensity after plasmonic sensitization due to the efficiently increasing emission at 450 nm. The interaction of LSPR with emission wavelength of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> is also taken into account through simulation of the electric field distributions of Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs with the optimum angle of 90° under different emission wavelengths excitation (Fig. S1, Supporting Information). The simulated

results show the dependence of electric field intensity on the extinction ability (Fig. 3i) and lower enhancement factors under emission wavelength excitation than that under 980 nm excitation. Therefore, the emission field has limited contribution to the enhancement of UCL.

In our case, the unique structure of Ag/W<sub>18</sub>O<sub>49</sub> composite film enables the Ag NRs to thoroughly contact the surface of the W<sub>18</sub>O<sub>49</sub> NWs, which also results in directly contact between the NaYF<sub>4</sub> NPs and plasmonic Ag/W<sub>18</sub>O<sub>49</sub>. The fluorescence quenching effect will happen due to the nonradiative energy transfer from emitters to plasmonic nanostructure [23,25,43], which consumingly relies on the distance between them [44,45]. The polyvinyl pyrrolidone K30 (PVP-K30, Mw = 44000-54000) polymer are applied as the insulating layer to isolate plasmonic Ag/W18O49 and NaYF4:Yb3+,Tm3+ components, thereby exploring the presence and suppression of the non-radiative energy transfer in the  $NaYF_4/Ag/W_{18}O_{49}$  composite film. To confirm the thickness of PVP spacer on the Ag NRs/W18O49 NWs surface, the TEM images of PVP-covered Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs are given in Fig. 7a. The thicknesses of PVP spacers increase gradually from 0 to 10 nm, meanwhile, the UCL properties for different thickness of intermediate layers change significantly (Fig. 7b). The UCL intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> is strengthened by introducing PVP spacer, and the maximum UC emission enhancement happens at the thickness of 2 nm. The UCL of NaYF<sub>4</sub> NPs in the composite film is further enhanced 3.2 times from  ${}^{1}D_{2}$ - ${}^{3}F_{4}$ ,  ${}^{1}G_{4}$ - ${}^{3}H_{6}$ , and <sup>1</sup>G<sub>4</sub>-<sup>3</sup>F<sub>4</sub> transitions with the optimum thickness of intermediate layer due to the suppressed non-radiative energy transfer (Fig. 7c). Finally, the overall UCL intensity of NaYF4:Yb<sup>3+</sup>, Tm<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> composite film is enhanced up to 938 times than that of the pure NaYF4: Yb<sup>3+</sup>, Tm<sup>3+</sup> NPs film. Furthermore, the lifetime decay of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> and NaYF<sub>4</sub> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film are investigated under 980 nm excitation (Fig. S2, Supporting Information). Comparing radiation transition rate after introducing the plasmonic layer, a small decrease of the average lifetime indicates the modulation on the spontaneous transition rate is minor. The UCL enhancement comes mainly from the interaction of LSPR with excitation electric field.

The  ${\rm Er}^{3+}$ -Yb<sup>3+</sup> dual-dopant composition is by far the most studied UC system, so the UCL of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs is investigated and optimized in the vicinity of the Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs composite film. A

similar significant enhancement is also observed via the dual LSPR effect as shown in Fig. 8. The UCL spectra of the comparative experiments in the existence of LSPR effect from NaYF4:Yb<sup>3+</sup>,Er<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> film show the typical green  $^2H_{11/2},\,^4S_{3/2},\,^4I_{15/2}$  and red  $\,^4F_{9/2},\,^4I_{15/2}$  transition transitions. As coupling with Ag/W<sub>18</sub>O<sub>49</sub> composite film, it is exciting to observe the enhancement up to 378 times, originating from 812 times in  ${}^{2}H_{11/2}$ - ${}^{4}I_{15/2}$ , 368 times in  ${}^{4}S_{3/2}$ - ${}^{4}I_{15/2}$  and 157 times in  ${}^{4}F_{9/2}$ - ${}^{4}I_{15/2}$ transitions respectively in optimum NaYF4:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs/Ag NRs/ W18O49 NWs composite film (Fig. 8a and b), and the micro-area photograph depicts a bright and spectacular green emission in the inset of Fig. 8a. Further introducing the insulating spacer enhances the UCL of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> Nps by suppressing nonradiative energy transfer (Fig. 8c). Finally, the enhancement for the overall UCL intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>/PVP/Ag/W<sub>18</sub>O<sub>49</sub> reaches 1221 times than the pure NaYF<sub>4</sub>:Yb<sup>3+</sup>.Er<sup>3+</sup> NPs. Based on the simulation and spectral results, we propose the mechanism of the UCL enhancement is attributed to the excitation enhancement created by the strengthen of localized electric field, which has been widely accepted. A dual LSPR coupling in an unusual combination of plasmonic metal with semiconductor nanostructures interacts strongly with excitation electric field, leading to large enhancement of localized excitation field strength.

LRET similar to fluorescence resonance energy transfer (FRET) is a mechanism, in which UCNPs are used as the energy donor, the UCL upon NIR excitation from UCNPs is transferred to acceptor molecules. The low UCL quantum yield is one of the bottleneck problems for the application of accurate molecules detection. Therefore, we explore a molecules detection system with a high sensitivity and a wide detecting range base on the NaYF<sub>4</sub>:Ln<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> composite film with remarkable UCL induced by dual LSPR modulation as shown in Fig. 9a. By varying the Ln<sup>3+</sup> dopants, LRET from multicolor UCL to different molecules, such as Rhodamine 6 G (R6 G), Rhodamin B (RhB), fluorescein isothiocyanate (FITC) etc, is realized by the donor emission spectrum overlapping with the acceptor absorption [46,47]. Herein, one detection system is using as example to support our concept, in which typical NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> UCNPs is selected as LRET donor with green emission band at 500-560 nm region, RhB fluorescent dye with optical absorption in range of 450-575 nm thus is chosen as acceptor (see Fig. 9b). The RhB with



**Fig. 7.** a) TEM images of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> treated by PVP spacer with the different thickness: (1) 0 nm, (2) 2 nm, (2) 5 nm, and (4) 10 nm. b) Upconversion emission spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> films with different PVP thicknesses. c) Enhancement factors of UCL as a function of the thickness of PVP spacer.



**Fig. 8.** a) Upconversion emission spectra and the corresponding micro-area optical images of (1) NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> film and (2) NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>/Ag/W<sub>18</sub>O<sub>49</sub> film. b) Histogram of enhancement factors of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs deposited on Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs substrate at the different emission wavelengths. c) Enhancement factors of UCL as a function of the thickness of PVP spacer in the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs/PVP/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film.



**Fig. 9.** a) The diagram of molecular detection process. b) Spectra of (1) emission spectrum from NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs excited at 980 nm, (2) the absorption and (3) emission spectra from of RhB stimulated by 540 nm. c) Emission spectra of RhB solution loaded with NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film. d) Integral areas of RhB as a function of its concentrations. e) Raman spectra of RhB solution containing different concentrations based on NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs/Ag NRs/W<sub>18</sub>O<sub>49</sub> NWs film. f) Correlation of SERS intensities of RhB at 1650 cm<sup>-1</sup> ranging from 10<sup>-9</sup> to 10<sup>-3</sup> mol/L.

different concentrations from  $10^{-3}$  to  $10^{-9}$  mol/L is prepared as fluorescence probe molecule. As shown in Fig. 9c, the emission peak of RhB solution ranging from 560 nm to 640 nm gradually increases with the increasing concentration of RhB solution alternately loaded on the NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> film, accompanied by the decrease of the green emission intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs. The results further confirm the existence of LRET. There has a good linear relationship between the RhB concentration and the integral area of RhB fluorescence emission under the stimulation of intense emission light (<sup>2</sup>H<sub>11/2</sub>·<sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub>·<sup>4</sup>I<sub>15/2</sub>) from NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> in the range of  $10^{-3}$ · $10^{-9}$  mol/L (Fig. 9d).

The SERS study is a spectroscopic technique for the detection of lowabundance analytes. Comparing with the LRET, SERS-based molecular detection can provide qualitative detection by providing fingerprint information with high sensitivity [48,49]. The plasmon-enhanced UCL is obtained in the NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> composite film, in the meanwhile it has no distinct suppression effect on the SERS signal. As shown in Fig. 9e, the SERS spectra of RhB solution on the surface of plasmonic NaYF<sub>4</sub>/Ag/W<sub>18</sub>O<sub>49</sub> film express characteristic vibrational features. The 400–2000 cm<sup>-1</sup> Raman shift window for 10<sup>-9</sup> to 10<sup>-3</sup> mol/L RhB concentrations is obtained, and the highest signal sensitivity Raman band at 1650 cm<sup>-1</sup> is selected for comparison among different RhB concentrations. The quantitative comparison of SERS intensities as a function of RhB concentration indicates a limited linear SERS response ranging from  $10^{-6}$  to  $10^{-9}$  mol/L as shown in Fig. 9f, which is similar to the reported literature on homogeneous SERS results recently. The narrow response-concentration window indicates the limitations of quantitative detection using SERS substrates comparing with LRET. The above results indicate that combining the LRET with SERS, it presents a new detect processing base on the plasmonic NaYF4/Ag/W18O49 composite film which is performed as the substrates for SERS and efficient upconversion fluorescence sensor simultaneously. We summarize recent representative sensors for the accurate determination of dye molecule by different ways, and the respective merits and limitations are listed in Table 1. The dual purpose sensor can offer two functionalities for molecular detection, the accurate quantitative detection by LRET in wide detecting range of 10<sup>-9</sup>-10<sup>-3</sup> M, and the qualitative detection by SERS with a highly qualitative limitation of RhB ( $10^{-9}$  M).

Table 1

A list of representative sensors for the accurate determination of dye molecule.

-						
Sensor type	Substrate	Analytes	Detection limit	Linear range	Qualitatively	Ref.
SERS sensors	Ag/TO-NFC nanopaper	RhB	$10^{-12} { m M}$	$10^{-12} \sim 10^{-9}\text{M}$	1	[50]
	Al-based WO <sub>3-x</sub>	R6 G	$10^{-8}$ M	$10^{-8} \sim 10^{-4} \ \text{M}$	1	[51]
Fluorescent sensors	NaYF4:Yb,Er/PS	R6 G	$2.1 imes10^{-8}~{ m M}$	$10^{-8} \sim 10^{-6} \ \text{M}$	X	[47]
	Au@SiO2	RhB	$2.1 imes10^{-8}~{ m M}$	$10^{-8} \sim 10^{-6} \ \text{M}$	X	[52]
Dual purpose sensor	NaYF4:Yb,Er/Ag/W18O49	RhB	$10^{-9}$ M	$10^{-9} \sim 10^{-3} \ \text{M}$	1	This work

#### 4. Conclusion

In this work, a dual plasmon-coupling hybrid film consisting of densely distributed Ag NRs loaded on W18O49 NWs substrate is welldesigned. The localized electric field in the vicinity of Ag/W18O49 composite film excited by incident light (980 nm) have been greatly magnified. By depositing self-assembly UCNPs onto Ag/W18O49 film surface, the remarkable UCL enhancement behavior of NaYF<sub>4</sub>:Ln<sup>3+</sup> NPs has been demonstrated through the employment of plasmonic-coupling effect. After optimizing the particle size of emitters and the thickness of insulated PVP spacer, the overall enhancement factors for the UCL intensity in the NaYF4:Yb,Tm/Ag/W18O49 up to 938-fold was acquired, 1221-fold enhancement in the NaYF4:Yb,Er/Ag/W18O49 is obtained similarly. The investigation indicates that the UCL enhancement mostly drive from the strong excitation field induced by dual LSPR-coupling of plasmonic. The NaYF4:Yb,Er/Ag/W18O49 luminescent composite film is successfully applied in the quantitative and qualitative RhB molecular detection by LRET and SERS, which is representative molecules detection system based on the NaYF<sub>4</sub>: $Ln^{3+}/Ag/W_{18}O_{49}$  composite film.

#### CRediT authorship contribution statement

Yang Yang: Investigation, Validation, Data curation, Writing original draft. Yan Cong: Writing - review & editing, Supervision. Jingyu Shang: Data curation, Formal analysis. Yang Liu: Data curation, Formal analysis. Guoqiang Fang: Data curation, Formal analysis. Jiahua Zhang: Conceptualization, Supervision. Bin Dong: Conceptualization, Supervision.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.129199.

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