

Article

Upconversion Luminescence of NaYF₄:Ln³⁺ Nanoparticles on Gold Nanorod Array with Dual-Wavelength Excitation

Haoyang Chen ^{1,2,†}, Xu Liu ^{1,2,†}, Xiangtai Xi ^{1,2}, Huan Chen ^{1,2}, Lei Yan ^{1,2}, Zhengkun Fu ^{1,2,*}, Jinping Li ^{1,2,*} and Zhenglong Zhang ^{1,2}

¹ School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, China; hychen@snnu.edu.cn (H.C.); xliu@snnu.edu.cn (X.L.); xixiangtai@snnu.edu.cn (X.X.); hchen@snnu.edu.cn (H.C.); yanlei@snnu.edu.cn (L.Y.); zlzhang@snnu.edu.cn (Z.Z.)

² Xi'an Key Laboratory of Optical Information Manipulation and Augmentation, Xi'an 710062, China

* Correspondence: zkfu@snnu.edu.cn (Z.F.); ljping@snnu.edu.cn (J.L.)

† These authors contributed equally to this work.

Abstract

Plasmonic nanostructures have been widely employed to improve upconversion luminescence performance; however, their impact on excitation pathways under multi-wavelength excitation is not yet fully understood. In this work, we constructed hybrid systems composed of gold nanorod arrays and NaYF₄:Yb³⁺/Ln³⁺ (Ln = Er³⁺, Tm³⁺) upconversion nanoparticles to systematically investigate upconversion behavior under dual-wavelength excitation at 808 and 976 nm. Contrary to the expected synergistic enhancement, our experimental results demonstrate that dual-wavelength excitation in the plasmonic hybrid structures produces different responses of upconversion emission. Measurements dependent on excitation power, along with the analysis of emission intensity ratio, indicate that plasmonic coupling under dual-wavelength excitation significantly enhances dissipative pathways that compete with upconversion processes. Notably, these effects strongly depend on the intrinsic energy-level structure of the lanthanide ions. In the Er³⁺-doped system, excitation at 808 nm facilitates population of higher-lying excited states, but the overall upconversion gain remains limited. In contrast, in the Tm³⁺-doped system, plasmonic coupling markedly amplifies stimulated emission and cross-relaxation processes, causing rapid depletion of high-energy state populations and substantial suppression of luminescence. These findings elucidate the competition between upconversion and dissipation processes governing plasmon-assisted upconversion under dual-wavelength excitation and provide a physical foundation for manipulating upconversion luminescence using multiple wavelengths.

Keywords: localized surface plasmon resonance; upconversion luminescence; gold nanorod array; dual-wavelength excitation; energy transfer

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1. Introduction

Rare-earth-doped upconversion nanoparticles (UCNPs) have attracted considerable attention due to their capability to convert low-energy near-infrared photons into visible or ultraviolet emission via multiphoton processes. Compared with conventional downconversion fluorescent materials, UCNPs enable near-infrared excitation, which offers advantages such as suppressed autofluorescence, deeper penetration depth, and

reduced photodamage, making them particularly attractive for bioimaging and photonic applications. [1–6]. These features make them highly promising for applications in anti-counterfeiting [7,8], photonic devices [9,10], and bioimaging [11–13]. Nevertheless, as the $4f$ – $4f$ electronic transitions in rare-earth ions are inherently forbidden, their absorption cross-sections are extremely small. Additionally, the stepwise multilevel energy-transfer processes involve substantial nonradiative losses, resulting in an overall low upconversion luminescence efficiency [14–16]. This intrinsic limitation considerably restricts their further development in advanced applications such as high-sensitivity detection, high-brightness displays, and efficient light–matter interactions, posing a major scientific challenge that remains to be overcome in the field of upconversion luminescence.

To overcome the aforementioned limitations in upconversion luminescence efficiency, researchers have developed a variety of strategies targeting the energy-level structures of rare-earth ions and the mechanisms of energy transfer. For example, the construction of core–shell heterostructures has been employed to suppress surface quenching [17–19], optimizing doping concentrations helps reduce cross-relaxation processes [15], and introducing sensitizer ions or organic dyes broadens absorption bandwidths. Additionally, excitation strategies have been adjusted to better match energy-transfer processes between different levels, while photonic crystals or metallic nanostructures have been utilized to modulate local electromagnetic field intensities. These approaches have all contributed, to varying degrees, to enhancing the luminescence performance of UCNPs. Among these, dual-wavelength excitation, as a unique strategy compared to traditional single-wavelength excitation, enables multidimensional control over emission peak, intensity, and dynamics by independently tuning the wavelengths [20], powers [21], and temporal sequences [22] of the two excitation beams, providing new opportunities for applications such as super-resolution imaging [23,24]. Meanwhile, plasmonic regulation strategies based on noble-metal nanostructures such as gold and silver [25,26] have attracted considerable attention in recent years because they can significantly amplify local electromagnetic fields [27,28] and modulate radiative and nonradiative decay channels. Plasmonic structures not only enhance the local intensity of the excitation light [29,30] but also influence the quantum yield and interlevel energy-transfer efficiency of UCNPs by regulating radiative [31] and nonradiative decay pathways [32], enabling a degree of controllable modulation over emission intensity and color. So far, dual-wavelength excitation strategies have been primarily applied to pure UCNPs systems, whereas most existing studies on plasmonic regulation are based on single-wavelength excitation, where the localized surface plasmon resonance (LSPR) linearly enhances a single excitation or emission process. By contrast, when multiple excitation wavelengths are introduced into plasmonic–upconversion hybrid systems, the coupling between local electromagnetic field enhancement, energy absorption, and multilevel energy transfer becomes significantly more complex, and the mechanisms governing their effects on upconversion luminescence and emission regulation remain largely unexplored.

In this work, a gold nanorod array with an LSPR peak in the near-infrared region was selected as the plasmonic substrate and combined with rare-earth-doped upconversion nanoparticles to construct a hybrid system. The variations in upconversion luminescence intensity, emission spectral distribution, and power-dependent behavior under dual-wavelength excitation were systematically investigated. By analyzing the emission intensities from different energy levels along with their corresponding power dependence exponents, the evolution of energy absorption and transfer mechanisms during the upconversion process was systematically examined. This study aims to elucidate the physical mechanisms of plasmon-assisted dual-wavelength excitation in upconversion luminescence systems, providing new physical insights and experimental guidance for the realization of highly efficient and tunable upconversion luminescence systems.

2. Materials and Methods

2.1. Materials

All reagents were purchased from commercial suppliers and were ready for use without further purification. Ytterbium acetate hexahydrate ($\text{Yb}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 6\text{H}_2\text{O}$, 99.99%), yttrium acetate hexahydrate ($\text{Y}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 6\text{H}_2\text{O}$, 99.99%), erbium acetate hexahydrate ($\text{Er}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 6\text{H}_2\text{O}$, 99.99%), thulium acetate hexahydrate ($\text{Tm}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 6\text{H}_2\text{O}$, 99.99%), 1-octadecene (1-ODE, 90%), oleic acid (OA, 90%), chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.9%), sodium oleate (NaOL, 97%), silver nitrate (AgNO_3 , 99%), and L-ascorbic acid (AA, 99.5%) were purchased from Sigma-Aldrich (Shanghai, China). Cyclohexane (C_6H_{12} , 99.7%), methyl alcohol (CH_3OH , 99.5%), ammonium fluoride (NH_4F , 96%), anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%), sodium hydroxide (NaOH , 96%), sodium borohydride (NaBH_4 , 99%), hydrochloric acid (HCl , 37% water), and cetyltrimethylammonium bromide (CTAB, 98.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Synthesis of Gold Nanorod

Synthesis of gold nanorods (AuNRs) was performed using the seed-mediated growth method [33]. First, 0.3645 g of CTAB was dissolved in 10 mL of deionized water. Then, 50 μL of 50 mM HAuCl_4 was added, turning the solution golden yellow. Next, 1 mL of 0.1 mM NaBH_4 was added under vigorous stirring to reduce the gold ions, forming the seed solution, which was left to stand at room temperature (25 °C) for 1 h. Subsequently, 0.7000 g of CTAB and 0.1234 g of NaOL were dissolved in 50 mL of deionized water at 50 °C until the solution became transparent. Once the solution cooled to 30 °C, 0.8 mL of 0.01 M AgNO_3 was added. After stirring the solution and allowing it to react for 15 min, 500 μL of 50 mM HAuCl_4 was added. The solution was stirred at 1400 rpm in a 30 °C water bath for 90 min. Afterward, 0.15 mL of 1 M HCl was added to adjust the pH, and the solution was stirred for an additional 15 min. Then, 125 μL of 0.1 M AA solution was added dropwise, and the solution was stirred for 1 min to obtain the growth solution. Finally, 80 μL of the seed solution was added to the growth solution and stirred for 1 min to ensure uniform mixing. The mixture was left to stand at 30 °C for 12 h for the growth of gold nanorods. After centrifugation, the AuNR product was obtained.

2.3. Preparation of Gold Nanorod Arrays

The gold nanorod arrays were prepared using the droplet evaporation self-assembly method [34]. First, the silicon wafers were cleaned by ultrasonic treatment with acetone and ethanol for 10 min and then dried in an oven for later use. Next, 10 mL of the gold nanorod solution synthesized by the seed-mediated growth method was centrifuged at 8000 rpm for 10 min. The supernatant was discarded, and the gold nanorods were dispersed in 2 mL of CTAB solution and sonicated for 10 min to achieve uniform dispersion. Then, 10 μL of the sonicated solution was dropped onto the cleaned silicon wafer. The wafer was then placed in a large glass bottle containing deionized water, and the bottle was sealed in a 30 °C constant-temperature environment. The wafer was left to stand for 12 h to allow the gold nanorods to self-assemble into a well-ordered array. Finally, the surface of the gold nanorod array was gently rinsed with deionized water to remove any residual impurities.

2.4. Synthesis of Upconversion Nanoparticles

Upconversion nanoparticles (UCNPs) were synthesized using the high-temperature thermal decomposition method as reported previously [35]. The specific process is as follows: 1.56 mmol of $\text{Y}(\text{C}_2\text{H}_3\text{O}_2)_3$, 0.40 mmol of $\text{Yb}(\text{C}_2\text{H}_3\text{O}_2)_3$, and 0.04 mmol of $\text{Er}(\text{C}_2\text{H}_3\text{O}_2)_3$ (or $\text{Tm}(\text{C}_2\text{H}_3\text{O}_2)_3$) were mixed with 30 mL of octadecene and 12 mL of oleic acid in a high-

temperature three-neck flask. The solution was continuously stirred at 800 rpm under a flow of argon gas. The flask was heated to 160 °C, forming a homogeneous solution, and kept at this temperature for 60 min, followed by cooling to 90 °C. Next, 5 mmol of NaOH and 8 mmol of NH_4F solids were separately dissolved in 10 mL of methanol and 20 mL of methanol. After the two solutions were mixed thoroughly, they were slowly added to the flask. The solution was then stirred at room temperature for 60 min. The solution was gradually heated to 60 °C and stirred for another 60 min to evaporate the methanol. To remove any remaining water in the solution, the mixture was vacuumed at 108 °C for 40 min. After vacuum treatment, the pressure was restored to normal, and the solution was heated to 305 °C under argon protection for 25 min. Finally, the solution was allowed to cool naturally under argon protection until it reached room temperature. The UCNPs were washed three times with ethanol and cyclohexane to obtain well-dispersed nanoparticles.

2.5. Fabrication of the AuNR–UCNP Hybrid Structure

The fabrication procedure of the AuNR–UCNP hybrid structure is schematically illustrated in Figure 1. The as-synthesized UCNPs were first diluted in cyclohexane to an appropriate concentration and ultrasonicated for 30 min to ensure uniform dispersion. Subsequently, a silicon substrate bearing the preassembled gold nanorod array was mounted on a spin coater and fixed under vacuum. A 10 μL aliquot of the diluted UCNPs solution was then drop-cast onto the center of the substrate. The spin-coating process was carried out in two steps: in the first step, the substrate was spun at 250 rpm for 10 s to allow the UCNPs to spread uniformly over the surface; in the second step, the spinning speed was increased to 1000 rpm and maintained for 40 s, enabling the formation of a quasi-monolayer of UCNPs under centrifugal force while accelerating solvent evaporation to prevent displacement of the gold nanorod array.

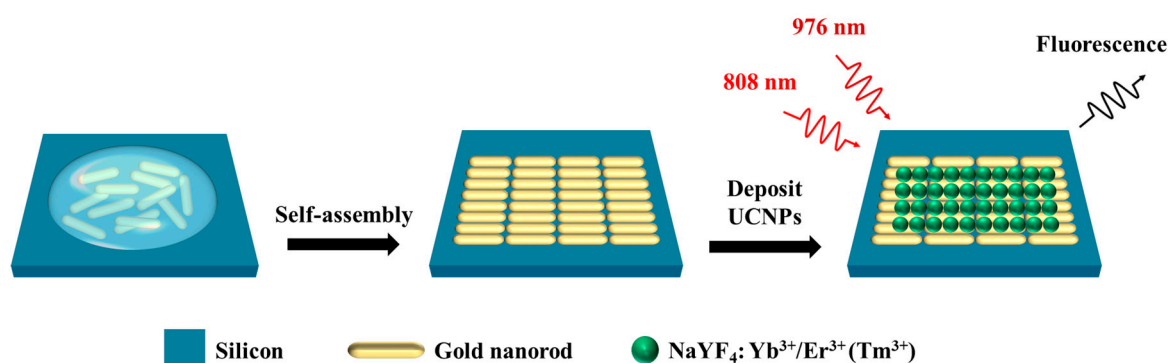


Figure 1. Schematic illustration of the experimental system.

2.6. Measurements of Upconversion Luminescence

The upconversion luminescence measurements were performed using a home-built confocal spectroscopic system. A simplified schematic of the optical setup is provided in Figure S3, including dual-wavelength excitation sources, polarization control, beam alignment, and spectral collection configuration. The detailed specifications of the optical components used are also provided in the Supporting Information.

3. Results and Discussion

3.1. Characteristics of the AuNR–UCNP Hybrid Structure

Figure 2 presents the structural and optical characterization of the AuNR–UCNP hybrid system investigated in this work. The SEM image in Figure 2a shows that the

synthesized gold nanorods exhibit good size uniformity and morphological consistency, with an average length of approximately 80 nm and a diameter of about 15 nm. The corresponding TEM image (Figure 2b) reveals a uniform low-contrast shell surrounding the gold nanorods, which originates from the cetyltrimethylammonium bromide (CTAB) molecular layer formed during synthesis. This CTAB shell not only stabilizes the nanorods but also provides an essential spatial separation between the metal surface and the luminescent centers in the hybrid structure, effectively suppressing nonradiative quenching caused by direct contact between the metal and the emitter [29,36].

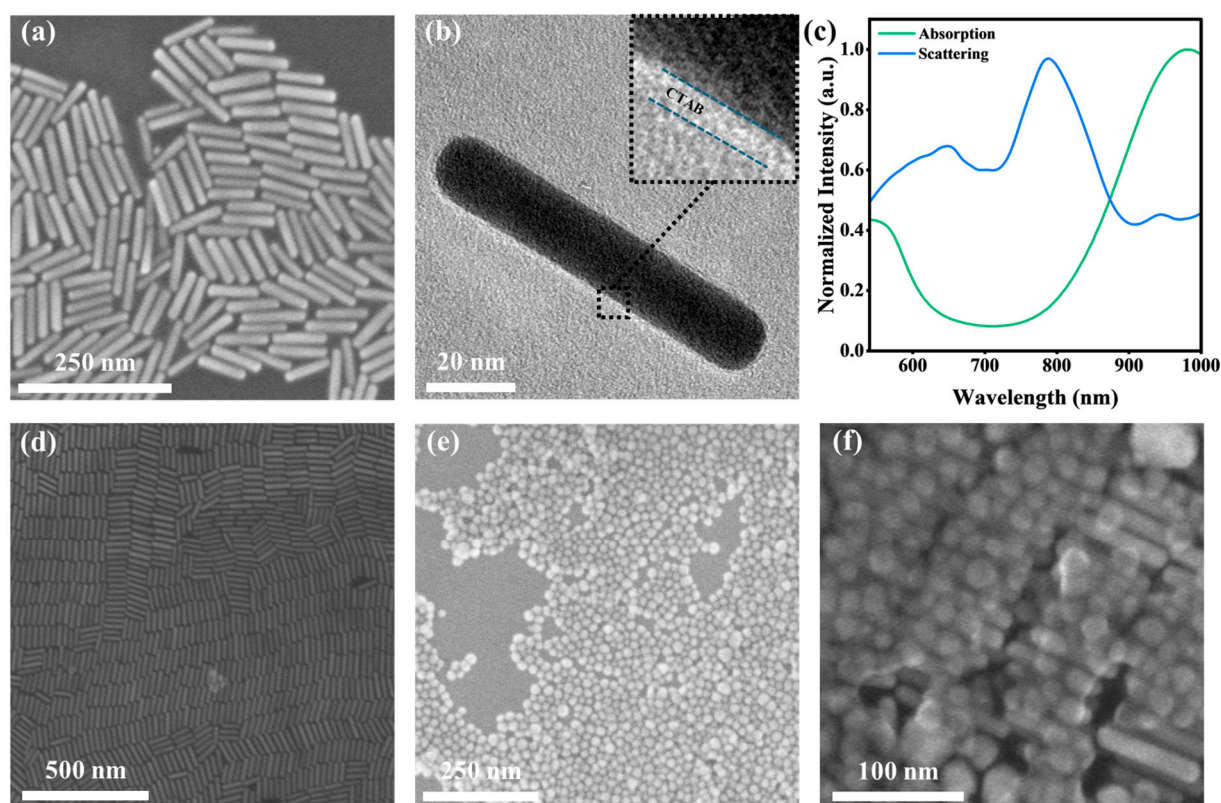


Figure 2. (a) SEM image of uniform gold nanorods; (b) TEM image of a single gold nanorod coated with a CTAB layer (the blue dashed lines); (c) normalized absorption spectrum of gold nanorods in aqueous solution (green line) and scattering spectrum of the horizontally aligned gold nanorod array (blue line); (d) SEM image of a horizontally aligned gold nanorod array; (e) SEM image of NaYF₄:Yb³⁺/Er³⁺ upconversion nanoparticles; (f) SEM image of the hybrid structure after spin-coating UCNP onto the assembled gold nanorod array.

The optical properties of the gold nanorods are shown in Figure 2c. During the seed-mediated growth process, parameters such as surfactant concentration, solution pH, and reactant concentration significantly influence the aspect ratio of the gold nanorods, which adjusts the position of the longitudinal localized surface plasmon resonance (LSPR) peak [33,37,38]. In this study, by precisely controlling the amount of silver nitrate added to 0.8 mL, gold nanorods with a longitudinal LSPR peak located around 980 nm in aqueous solution were obtained (green curve in Figure 2c). The gold nanorods were subsequently assembled onto the silicon substrate using a droplet evaporation self-assembly method [34]. After self-assembly, the surrounding medium of the gold nanorods changes from water to air, leading to a decrease in the effective refractive index. Consequently, the LSPR peak in the dark-field scattering spectrum exhibits a pronounced blue shift to approximately 808 nm (blue curve in Figure 2c), which aligns well with the 808 nm excitation wavelength employed in this work. Figures 2d and S1 show large-area, well-ordered gold

nanorod arrays formed by the droplet evaporation self-assembly method, which provide a high-quality substrate for the subsequent experiments.

Figure 2e shows the SEM image of the NaYF₄:Yb³⁺/Er³⁺ UCNPs synthesized by a high-temperature thermal decomposition method, exhibiting a uniform size distribution with an average particle diameter of approximately 16 nm, as further quantified by the particle size histograms shown in Figure S4. High-resolution TEM images (Figure S5) reveal clear lattice fringes with an interplanar spacing of approximately 0.302 nm, consistent with the (101) planes of hexagonal β -NaYF₄, confirming the formation of the highly efficient up-conversion crystal phase. The AuNR–UCNP hybrid structure formed after depositing the UCNPs onto the AuNRs is shown in Figure 2f. The UCNPs are uniformly distributed over the array surface and form a compact yet noncontact coupling configuration with the gold nanorods, providing an appropriate structural basis for subsequent investigations of plasmon-assisted regulation of upconversion luminescence under dual-wavelength excitation.

3.2. Er³⁺-Doped Hybrid System with Dual-Wavelength Excitation

Initially, we recorded the upconversion luminescence spectra of NaYF₄:20%Yb³⁺/2%Er³⁺ UCNPs on both silicon substrates and AuNR substrates under three different excitation conditions: single-wavelength excitation at 808 nm, single-wavelength excitation at 976 nm, and dual-wavelength excitation combining 976 nm and 808 nm, as shown in Figure 3a,b.

On the silicon substrate, excitation with an 808 nm laser did not produce any detectable luminescence, which is attributed to the mismatch between the Yb³⁺ energy levels and the 808 nm laser, as well as the extremely small absorption cross-section of Er³⁺ at 808 nm. When excited with a 976 nm laser, the typical upconversion luminescence of Er³⁺ was observed. Under dual-wavelength excitation on the Silicon substrate, a significant increase in luminescence intensity was observed (blue curve in Figure 3a), indicating a synergistic effect between the two excitation wavelengths that increases the population rate of excited states through cooperative energy transfer (ET) and excited-state absorption (ESA) assisted pathways, thereby enhancing the overall emission intensity. We further compared the integrated intensity ratios of red (~655 nm, corresponding to the ⁴F_{9/2}→⁴I_{15/2} transition), green (~540 nm, ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2}), and blue (~410 nm, ²H_{9/2}→⁴I_{15/2}) emissions under 976 nm single-wavelength and dual-wavelength excitations, as shown in Figure 3c,d. The red-to-green ratio increased from 1.91 to 2.29, while the red-to-blue ratio increased from 8.91 to 16.38. As illustrated in the energy-level diagram of NaYF₄:Yb³⁺/Er³⁺ in Figure 3e, when excited with a single wavelength of 976 nm, Yb³⁺ ions act as a sensitizer by efficiently absorbing photons through the ²F_{7/2}→²F_{5/2} transition and subsequently transferring the energy to neighboring Er³⁺ ions. Here, ET1 refers to the primary Yb³⁺→Er³⁺ energy-transfer process that promotes Er³⁺ ions from the ground state ⁴I_{15/2} to the intermediate level ⁴I_{11/2}, serving as the initial population channel for all upconversion pathways in the Er³⁺-doped system. The ⁴I_{11/2} level subsequently relaxes non-radiatively to the ⁴I_{13/2} level. Following this, the ET2 process excites Er³⁺ ions from ⁴I_{13/2} to ⁴F_{9/2}, which gives rise to the red emission at ~655 nm through the ⁴F_{9/2}→⁴I_{15/2} transition. The ET3 (²F_{5/2}(Yb³⁺) + ⁴I_{11/2}(Er³⁺)→²F_{7/2}(Yb³⁺) + ⁴F_{7/2}(Er³⁺)) and ET4 (²F_{5/2}(Yb³⁺) + ⁴F_{9/2}(Er³⁺)→²F_{7/2}(Yb³⁺) + ²H_{9/2}(Er³⁺)) processes contribute predominantly to the green and blue emissions, respectively. Upon introducing the 808 nm excitation, additional pumping pathways are activated in the system, including ground-state absorption (GSA, ⁴F_{15/2}→⁴I_{9/2}), excited-state absorption ESA1 (⁴I_{13/2}→⁴F_{9/2}/⁴S_{3/2}), and ESA2 (⁴I_{9/2}→²H_{9/2}) [39]. For the red and green emissions originating from intermediate energy levels, although the intrinsic absorption cross-section of Er³⁺ at 808 nm is relatively small, the weak GSA and ESA1 processes act synergistically with the energy-transfer processes ET1 and ET2, accelerating the population transfer between the

ground state and intermediate excited states and thereby enhancing the overall emission intensity. As a result, the red-to-green intensity ratio exhibits only a slight increase, from 1.91 to 2.29, due to the nearly synchronous population variation in the intermediate levels. In contrast, because the ESA2 process depends on the population of the intermediate energy levels, its contribution is much weaker than that of GSA and ESA1, resulting in only a limited enhancement of the blue emission. Consequently, the red-to-blue intensity ratio increases markedly, from 8.91 to 16.38 (Figure 3c,d).

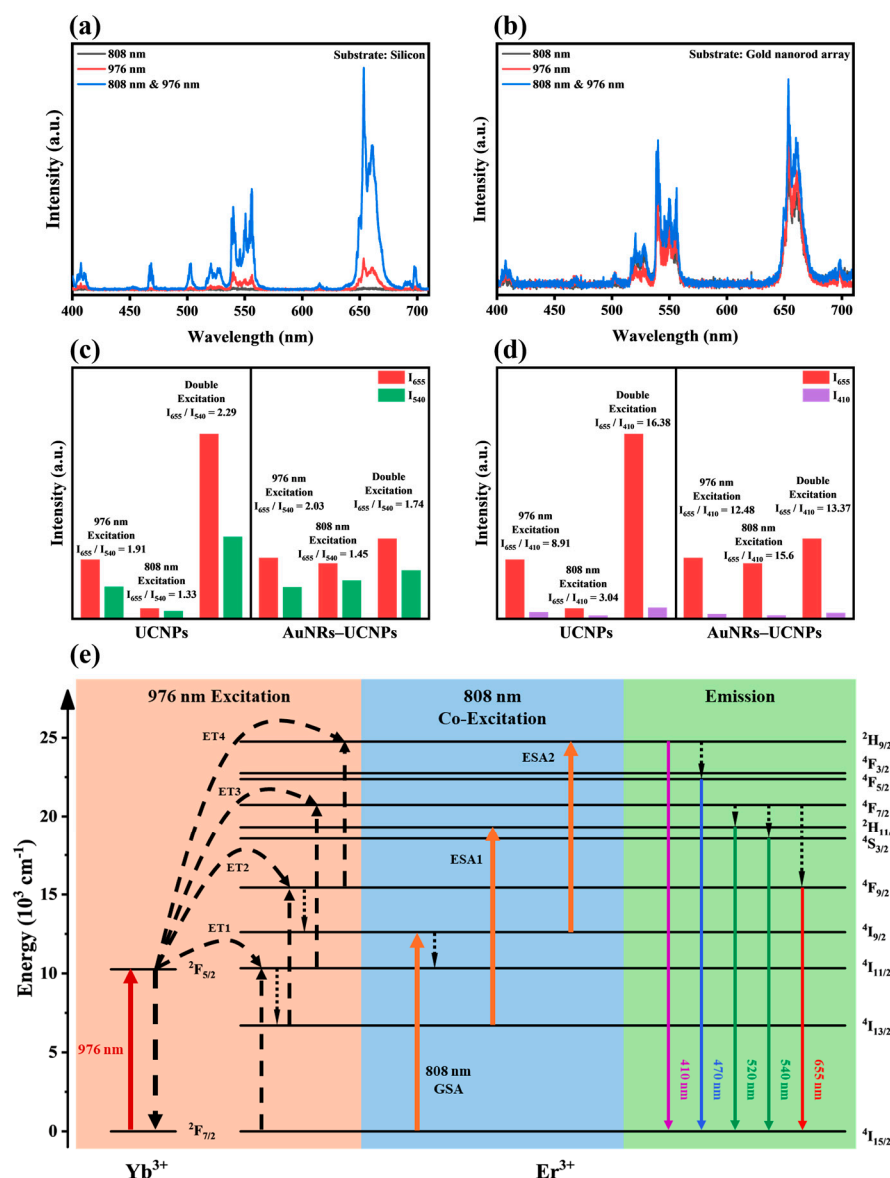


Figure 3. (a,b) Upconversion luminescence spectra of NaYF₄:Yb³⁺/Er³⁺ on Si and AuNR substrates under single- and dual-wavelength excitation, where the gray line represents excitation at 808 nm, the red line represents excitation at 976 nm, and the blue line represents dual-wavelength excitation ($P_{976\text{ nm}} = 2\text{ mW}$, $P_{808\text{ nm}} = 30\text{ mW}$, integration time = 0.1 s); (c,d) variation in the integrated intensity ratios of 655 nm, 540 nm, and 410 nm emissions from Er³⁺ under different excitation schemes and on different substrates; the integration ranges are 400–420 nm, 530–560 nm, and 630–680 nm; (e) schematic diagram of the energy-transfer process in NaYF₄:Yb³⁺/Er³⁺ under dual-wavelength excitation.

In the AuNR–NaYF₄:Yb³⁺/Er³⁺ hybrid system, the upconversion luminescence process exhibits unique characteristics under dual-wavelength excitation that are markedly different from those observed on a silicon substrate (Figure 3b). When the 808 nm laser is applied, the longitudinal localized surface plasmon resonance (LSPR) peak of the horizontally aligned gold nanorod array precisely resonates with the excitation wavelength, which is further confirmed by the simulated local electric field enhancement distributions obtained using COMSOL Multiphysics 6.2, showing significantly stronger near-field intensities at 808 nm compared with 976 nm (Figure S2). This spectral matching increases the local electromagnetic field experienced around the upconversion nanoparticles [40,41], allowing a clearly distinguishable upconversion luminescence signal to be observed under single-wavelength excitation at 808 nm. Meanwhile, under single-wavelength excitation at 976 nm, the sample exhibits the characteristic Er³⁺ upconversion emission features, confirming that 976 nm excitation retains its dominant role as the primary energy input pathway in the hybrid system. Notably, when both 808 nm and 976 nm lasers are used simultaneously, the overall upconversion luminescence intensity shows only slightly increases compared with single 976 nm excitation and is markedly weaker than the enhancement trend observed on the silicon substrate. Moreover, the intensities of certain emission bands appear to be constrained.

The observations of dual-wavelength excitation in the hybrid system indicate that the plasmon-enhanced local electromagnetic field plays a dual role in the hybrid system. On the one hand, it boosts the effective absorption probability of Er³⁺-related transitions at 808 nm, including both weak ground-state absorption (GSA, ⁴F_{15/2}→⁴I_{9/2}) and excited-state absorption processes (ESA1 and ESA2) [42]. The enhancement of the ESA1 process, which is directly associated with the green emission, promotes the green luminescence intensity and partially depletes the population contributing to the red-emitting transitions, resulting in a slight decrease in the red-to-green intensity ratio. Meanwhile, the activation of the ESA2 pathway effectively enhances the pathway toward high-lying excited states, leading to a pronounced increase in the high-energy-level population and consequently an enhancement of the blue emission. As a result, the increase in the red-to-blue ratio (from 12.48 only to 13.37) is substantially reduced compared with that observed on the silicon substrate (Figure 3c,d). On the other hand, the plasmonic effects from the AuNRs are inevitably accompanied by additional energy dissipation channels, including the acceleration of multiphoton nonradiative relaxation and plasmon-mediated photothermal dissipation [43]. The competition between enhanced absorption and these dissipation pathways shifts the balance toward rapid energy loss, thereby suppressing the steady-state population of emissive excited states and ultimately leading to a pronounced reduction in the overall upconversion luminescence under dual-wavelength excitation.

To analyze its nonlinear behavior, we monitored upconversion luminescence intensity as a function of the excitation power for the AuNR–UCNP hybrid system via dual-wavelength excitation. When the excitation power at 976 nm was fixed, and the power at 808 nm was gradually increased, the power-dependent exponents (*n* values) of the red and green emissions decreased to values close to zero or even became negative, whereas the blue emission exhibited only a weak positive dependence (Figure 4a). Correspondingly, the red-to-green intensity ratio showed only a marginal increase, while the red-to-blue ratio decreased markedly with increasing 808 nm power (Figure 4b). In contrast, when the 808 nm power was fixed, and the 976 nm excitation power was increased, the power exponents of the red and green emissions recovered to approximately 0.5, and the exponent of the blue emission increased to about 0.66 (Figure 4c). Nevertheless, compared with conventional single-wavelength excitation, the *n* values of all emission bands remained noticeably compressed, and the evolution of the intensity ratios exhibited distinct characteristics: the red-to-green ratio remained nearly constant, whereas the red-to-blue

ratio decreased more obviously with increasing 976 nm power (Figure 4d). These observations suggest that 976 nm excitation remains the dominant energy input channel driving the Er^{3+} upconversion process in the hybrid system. In addition, excitation at 808 nm, when combined with plasmonic resonance, mainly helps reach higher excited states by enhancing the ESA2 pathway. This, in turn, allows for a relative increase in emissions from higher energy levels. Meanwhile, the upconversion process is consistently affected by plasmon-related dissipative pathways, which effectively limit the enhancement of the overall emission intensity. Time-resolved decay measurements at 655 nm (Figure S6a) further reveal a shortened emission lifetime in the hybrid structure, indicating plasmon-induced acceleration of nonradiative relaxation processes.

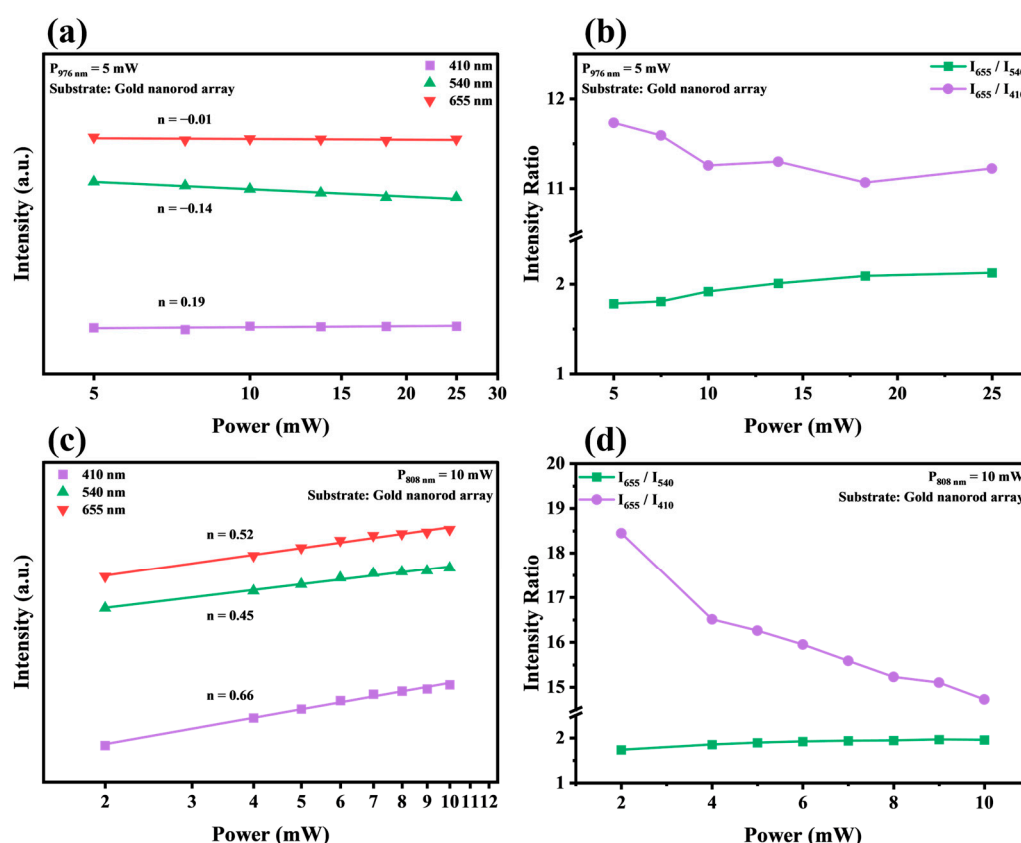


Figure 4. Upconversion luminescence characteristics of the AuNR-NaYF₄:Yb³⁺/Er³⁺ hybrid structure under dual-wavelength excitation. With the 976 nm laser power fixed at 5 mW and the 808 nm laser power gradually increased, (a) the emission intensities of blue (~410 nm), green (~540 nm), and red (~655 nm) bands together with their fitted power dependence exponents, and (b) the evolution of the red-to-green (655 nm/540 nm) and red-to-blue (655 nm/410 nm) intensity ratios were determined. With the 808 nm laser power fixed at 10 mW and the 976 nm laser power gradually increased, we also analyzed (c) the emission intensities of the blue (~410 nm), green (~540 nm), and red (~655 nm) bands together with their fitted power dependence exponents, and (d) the corresponding red-to-green and red-to-blue intensity ratios.

Based on the above experimental results, it can be concluded that in the dual-wavelength-excited AuNR-NaYF₄:Yb³⁺/Er³⁺ UCNP hybrid structure, the upconversion luminescence is still predominantly driven by the 976 nm laser, whereas the 808 nm laser mainly influences the upconversion process within the plasmon-coupled environment. The localized surface plasmon resonance of the AuNRs at 808 nm enhances the local electromagnetic field, which enables the otherwise weak 808 nm excitation process and increases the probability of Er^{3+} transitions to higher excited states via pathways such as

ESA1 and ESA2. However, plasmonic coupling also causes significant local heating and accelerates multiphonon nonradiative relaxation processes [40,44], leading to an increase in the dissipative pathways. As a result, there is a competition between the 808 nm-induced population of high-energy levels and the plasmon-enhanced nonradiative dissipation [45], so the overall luminescence intensity does not increase significantly. These findings indicate that in dual-wavelength-excited plasmon-upconversion nanoparticle hybrid systems, the plasmonic effect governs the upconversion luminescence by restructuring the balance between radiative excitation and nonradiative dissipation pathways.

3.3. Tm^{3+} -Doped Hybrid System with Dual-Wavelength Excitation

To further investigate the effects of dual-wavelength excitation on the AuNR-UCNP hybrid structure, $\text{NaYF}_4\text{:}20\%\text{Yb}^{3+}/2\%\text{Tm}^{3+}$ UCNPs were used to prepare analogous samples. Their upconversion luminescence spectra, integrated intensity ratios, and power-dependent characteristics were measured using the same methods, as illustrated in Figures 5 and 6.

For $\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$ nanoparticles, dual-wavelength excitation on both Si (Figure 5a) and AuNR substrates (Figure 5b) resulted in luminescence suppression, with a stronger effect observed in the AuNR-UCNP hybrid structure. Comparing the integrated intensity ratios of the characteristic emission peaks at 455 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_4$), 478 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$), and 650 nm ($^1\text{G}_4 \rightarrow ^3\text{F}_4$), it was observed that the introduction of the 808 nm laser led to a continuous decrease in I_{455}/I_{478} and I_{455}/I_{650} ratios on both Si and AuNR substrates. Specifically, on the Si substrate, I_{455}/I_{478} decreased from 5.16 to 3.24, and I_{455}/I_{650} decreased from 9.74 to 7.30. In comparison, a more pronounced reduction occurred on the AuNR substrate, where I_{455}/I_{478} dropped sharply from 5.21 to 2.86, and I_{455}/I_{650} decreased from 9.77 to 6.17 (Figure 5c,d). These results indicate that, under dual-wavelength excitation, the population of particles in the high-energy $^1\text{D}_2$ state is effectively diminished, promoting energy redistribution toward lower-energy states.

In further analyzing the power-dependent characteristics under dual-wavelength excitation, the laser power at 976 nm was fixed at 5 mW, while the power at 808 nm was gradually increased (Figure 6). On the Si substrate (Figure 6a), the emission intensities at 455 nm, 478 nm, and 650 nm exhibit clear piecewise behavior. As a representative case, the characteristic blue emission at 455 nm is discussed. When the 808 nm power was relatively low (<5 mW), the power dependence exponent (n value) was approximately 0.14, indicating that the inhibitory effect of the 808 nm laser on the upconversion process was still negligible, and the system was in a transitional energy-competition state. As the 808 nm power increased to approximately 5–12 mW, the fitted n values gradually changed from near zero to negative, suggesting that the 808 nm excitation began to introduce effective energy dissipation channels. When the 808 nm power was further increased (>12 mW), the n value rapidly decreased to -0.49 , indicating a significant suppression of the 455 nm emission. Based on the energy-level diagram of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$ (Figure 5e), it can be seen that upon the introduction of 808 nm excitation, Tm^{3+} ions engage in ground-state absorption (GSA, $^3\text{H}_6 \rightarrow ^3\text{H}_4$) and excited-state absorption (ESA, $^3\text{H}_5 \rightarrow ^1\text{G}_4$), which begin to play a significant role. At relatively low 808 nm power, ESA can weakly assist the population of higher excited states in cooperation with Yb^{3+} -sensitized ET processes. However, at higher 808 nm power densities, a stimulated emission process from the $^1\text{D}_2$ level to the $^3\text{F}_2$ level becomes significant [46]. Since the $^1\text{D}_2$ level serves as the upper emitting state for the 455 nm transition ($^1\text{D}_2 \rightarrow ^3\text{F}_4$), the stimulated depletion of $^1\text{D}_2$ directly competes with radiative emission, resulting in a pronounced suppression of the 455 nm upconversion luminescence. This behavior is supported by the negative power dependence observed in the experiments and is characteristic of a STED-like depletion process in the Tm^{3+} system.

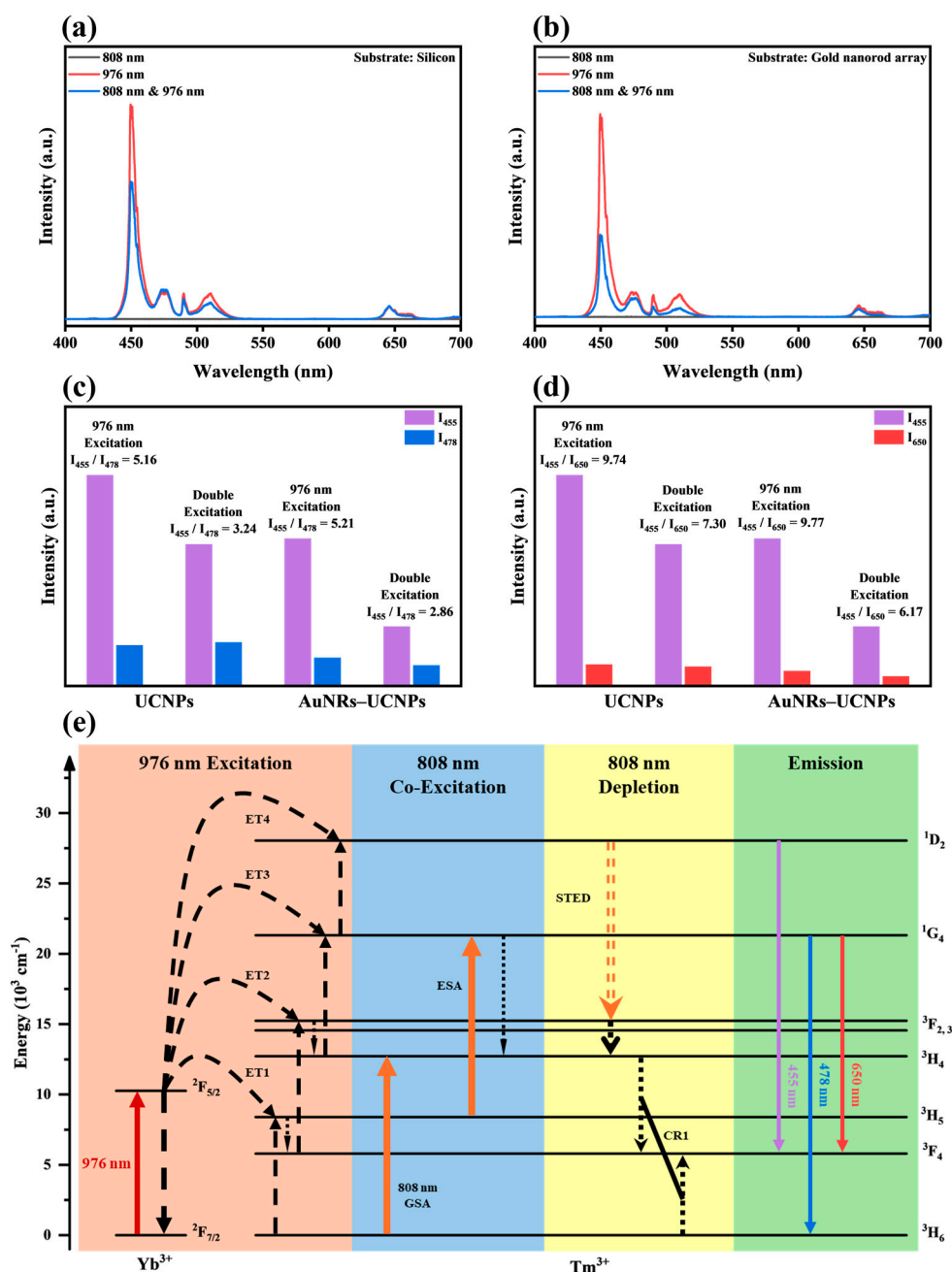


Figure 5. (a,b) Upconversion luminescence spectra of NaYF₄:Yb³⁺/Tm³⁺ on Si and AuNR substrates under single- and dual-wavelength excitation, where the gray line represents excitation at 808 nm, the red line represents excitation at 976 nm, and the blue line represents dual-wavelength excitation ($P_{976\text{ nm}} = 5\text{ mW}$, $P_{808\text{ nm}} = 10\text{ mW}$, integration time = 0.1 s); (c,d) variations in the integrated intensity ratios of Tm³⁺ emissions at 455 nm, 478 nm, and 650 nm under different excitation schemes and on different substrates; the integration ranges are 430–465 nm, 465–490 nm, and 630–680 nm; (e) schematic diagram of the energy-transfer process in NaYF₄:Yb³⁺/Tm³⁺ under dual-wavelength excitation.

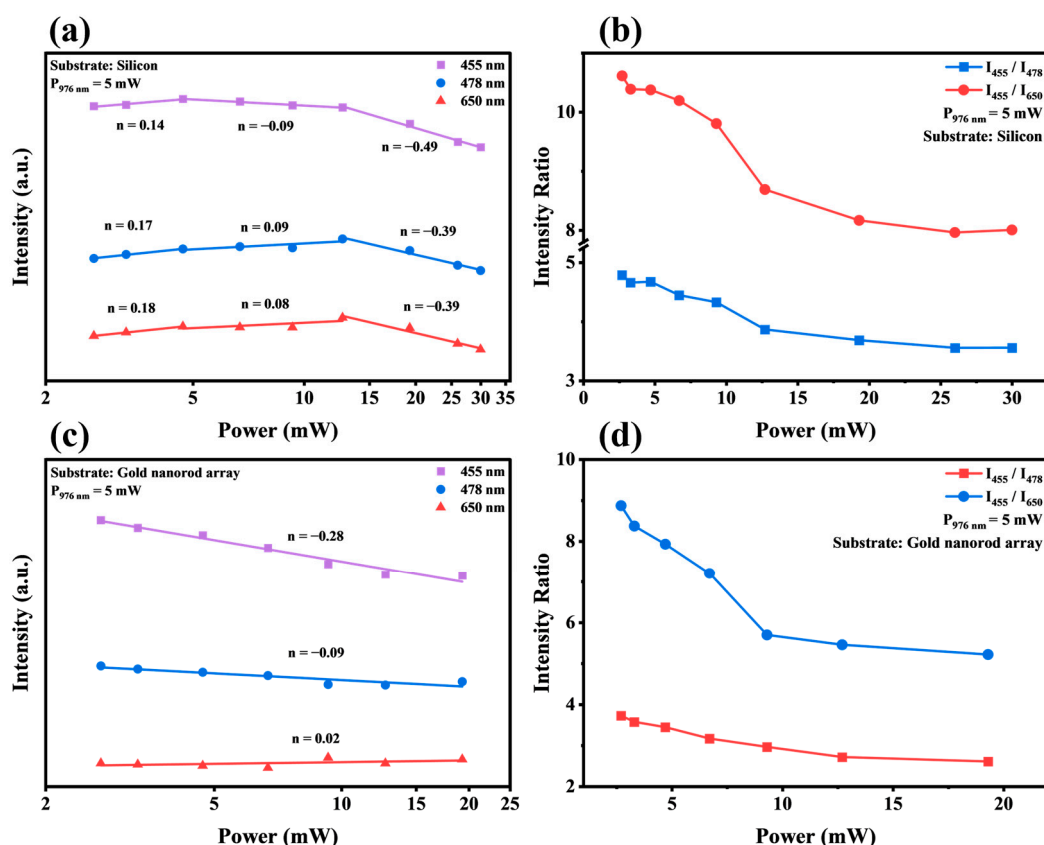


Figure 6. (a,c) Power-dependent emission intensities at 455 nm, 478 nm, and 650 nm, together with the corresponding fitted power-law exponents, measured on the silicon (a) and the AuNR substrate (c), respectively; (b,d) variations in the integrated intensity ratios of 455 nm/478 nm and 455 nm/650 nm as a function of excitation power on the silicon substrate (b) and the AuNR substrate (d).

The AuNR–NaYF₄:Yb³⁺/Tm³⁺ hybrid structure exhibits a markedly stronger suppression of upconversion luminescence under dual-wavelength excitation (Figure 5b). This effect mainly stems from the unique and densely spaced energy-level structure of Tm³⁺ ions, which renders them highly susceptible to plasmonic modulation. Unlike the Er³⁺ system, where 808 nm excitation mainly assists the population of intermediate states, in the Tm³⁺ system, the plasmon-enhanced 808 nm field preferentially couples to 808 nm-related transitions, including stimulated emission depletion and cross-relaxation pathways, due to the unique energy level structure of Tm³⁺. In this system, excitation at 976 nm mainly proceeds via Yb³⁺ sensitization, stepwise promoting Tm³⁺ ions from the ground state to higher-lying levels such as ¹G₄ and ¹D₂, which produce the characteristic upconversion emissions at 478 nm and 455 nm, respectively. However, when an 808 nm laser is introduced, and plasmonic coupling with the gold nanorod array is established, the energy-transfer pathways of the system are fundamentally restructured. The plasmon-enhanced local electromagnetic field substantially amplifies the light–matter interaction of Tm³⁺ ions at 808 nm, rendering the stimulated emission process from the ¹D₂ level to the ³F₂ level highly efficient even at relatively low excitation powers [46]. Because the ¹D₂ level serves as the upper emitting state for the 455 nm transition, this stimulated emission competes directly with the radiative process, leading to rapid depletion of the high-energy emissive states. The shortened lifetime of the 455 nm emission observed in Figure S6b further indicates that the plasmonic effect accelerates the radiative decay rate. This mechanism is further corroborated by the results shown in Figure 6c, where the 455 nm emission intensity in the AuNR–UCNP hybrid structure decreases monotonically as the 808 nm excitation

power increases, which contrasts sharply with the segmented power-dependent behavior observed on the silicon substrate.

Concurrently, the plasmon-enhanced local field, together with the associated photo-thermal effects, significantly intensifies cross-relaxation processes among Tm^{3+} ions, particularly CR1 ($^1\text{D}_2 + ^3\text{H}_6 \rightarrow ^3\text{F}_4 + ^3\text{F}_4$), thereby further driving the population distribution toward lower-energy states [46,47]. This process not only accelerates the depletion of high-energy populations but also introduces additional nonradiative energy-loss channels into the system. A comparison of the emission intensity ratios at 455 nm/478 nm and 455 nm/650 nm (Figure 6b,d) clearly shows that both ratios decrease monotonically with increasing 808 nm excitation power. Notably, in the AuNR–UCNP hybrid structure, a more pronounced reduction in these ratios is observed at low excitation powers, indicating that plasmonic resonance substantially enhances energy dissipation pathways in the system. These observations further indicate that, under dual-wavelength excitation, the combined action of stimulated emission and cross-relaxation induces an overall collapse of the population distribution toward lower-energy levels. In summary, within the AuNR– $\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$ hybrid system, localized surface plasmon effects substantially amplify the luminescence suppression mechanism under dual-wavelength excitation and significantly lower the power threshold required for the onset of suppression.

4. Conclusions

In this work, a plasmonic gold nanorod array–upconversion nanoparticle (AuNR–UCNP) hybrid system was constructed to systematically investigate the competitive behavior of plasmon-assisted upconversion processes under dual-wavelength excitation at 808 nm and 976 nm. For the $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ system, the plasmon-enhanced local electromagnetic field selectively modulates the relative contributions of specific excitation pathways, thereby changing the population of different energy levels. At the same time, it speeds up energy dissipation, which leads to a limited overall emission gain accompanied by changes in the relative emission intensities. In contrast, for the $\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$ system, plasmonic coupling markedly amplifies stimulated emission depletion and cross-relaxation processes under 808 nm excitation, leading to a rapid depopulation of high-energy states toward lower-lying levels and giving rise to pronounced suppression of upconversion luminescence under dual-wavelength excitation.

These findings reveal that, in multi-wavelength-excited upconversion systems, plasmons act not merely as optical field enhancement factors but instead play a decisive role in governing energy competition and emission regulation through their coupling with the intrinsic energy-level structures of rare-earth ions. This study provides an experimental foundation for understanding complex energy-transfer mechanisms in multi-wavelength plasmon–upconversion coupled systems and offers important insights for the design of wavelength-selective and emission-tunable nanophotonic devices.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano16040277/s1>, Figure S1: Large-area gold nanorod arrays formed by the droplet evaporation self-assembly method; Figure S2: Simulated local electric field distributions of the gold nanorod array under excitation at 808 nm and 976 nm with different polarization (a–b) The polarization direction is parallel to the short axis of the AuNRs; (c–d) the polarization direction is parallel to the long axis of the AuNRs; Figure S3: Simplified schematic diagram of the optical spectroscopic measurement system; Figure S4: Size distribution histogram of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ (a) and $\text{NaYF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}$ (b) upconversion nanoparticles; Figure S5: HRTEM image of the UCNPs; Figure S6: Fluorescence decay curve at (a) 655 nm of Er^{3+} and (b) 455 nm of Tm^{3+} measured using the TCSPC method.

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Abbreviations

The following abbreviations are used in this manuscript:

AuNRs	Gold nanorod arrays
UCNPs	Upconversion nanoparticles
LSPR	localized surface plasmon resonance
STED	Stimulated emission depletion

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