Near-Infrared-Plasmonic Energy Upconversion in a Nonmetallic Heterostructure for Efficient $H_2$ Evolution from Ammonia Borane

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Plasmonic metal nanostructures have been widely used to enhance the upconversion efficiency of the near-infrared (NIR) photons into the visible region via the localized surface plasmon resonance (LSPR) effect. However, the direct utilization of low-cost nonmetallic semiconductors to both concentrate and transfer the NIR-plasmonic energy in the upconversion system remains a significant challenge. Here, a fascinating process of NIR-plasmonic energy upconversion in Yb$^{3+}$/Er$^{3+}$-doped NaYF$_4$ nanoparticles (NaYF$_4$:Yb-Er NPs)/W$_{18}$O$_{49}$ nanowires (NWs) heterostructures, which can selectively enhance the upconversion luminescence by two orders of magnitude, is demonstrated. Combined with theoretical calculations, it is proposed that the NIR-excited LSPR of W$_{18}$O$_{49}$ NWs is the primary reason for the enhanced upconversion luminescence of NaYF$_4$:Yb-Er NPs. Meanwhile, this plasmon-enhanced upconversion luminescence can be partly absorbed by the W$_{18}$O$_{49}$ NWs to re-excite its higher energy LSPR, thus leading to the selective enhancement of upconversion luminescence for the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ heterostructures. More importantly, based on this process of plasmonic energy transfer, an NIR-driven catalyst of NaYF$_4$:Yb-Er NPs@W$_{18}$O$_{49}$ NWs quasi-core/shell heterostructure, which exhibits a ≈35-fold increase in the catalytic $H_2$ evolution from ammonia borane (BH$_3$NH$_3$) is designed and synthesized. This work provides insight on the development of nonmetallic plasmon-sensitized optical materials that can potentially be applied in photocatalysis, optoelectronic, and photovoltaic devices.

Over the past several decades, the fascinating photophysical phenomena of localized surface plasmon resonance (LSPR) have attracted significant interests in research areas such as electronics, photonics, and catalysis. This is mainly due to their unique capability to concentrate and amplify the incident light intensity near the surface of plasmonic nanostructures.[1–3] As a classic plasmonic “optical antenna,” noble metal nanostructures with tunable LSPR energy are frequently introduced into nanomaterials to promote their performance in light absorption and/or emission via plasmonic energy transfer from noble metal to neighboring optical nanomaterials.[4–6] For example, coupling appropriate nanostructures of plasmonic Au or Ag with upconversion nanoparticles, in particular trivalent lanthanide ions (Ln$^{3+}$)-doped NaYF$_4$ nanoparticles (NPs), can achieve enhanced upconversion luminescence in the visible light region by converting lower frequency incident photons at 980 nm with high effectivity.[7–9] This paradigm has been regarded as a promising tactic to use the low-energy NIR light, which makes up almost half of the solar energy (≈40%), in the field of solar-to-fuels energy conversion.[10,11] From a plasmonic point of view, the overlapping spectra between LSPR bands of noble metals and the excitation/emission bands of upconversion NPs would result in a highly efficient upconversion of NIR to visible light.[12,13] Although some specific metallic structures, such as long nanowires (NWs) and nanoforest, can easily provide a very wide band for simultaneously matching the excitation

Plasmonic Semiconductors

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and emission bands of Ln³⁺-doped NaYF₄ NPs, manipulating the shapes and sizes of these metallic structures often requires a very complex synthesis process.[14,15] Furthermore, using noble metals inevitably suffers from high cost and earth rarity. Therefore, exploiting noble-metal-free tractable plasmonic nanostructures to sensitize the upconversion luminescence of Ln³⁺-doped NaYF₄ NPs is of great significance for boosting the development of NIR-driven energy generation.

Recently, some researches have reported that the LSPR phenomena can also occur on various nonmetal nanostructures of heavily doped nonstoichiometric semiconductors, such as Cu₂₋ₓS, Sn-doped In₂O₃, WO₃₋ₓ, and MoO₃₋ₓ.[16–20] LSPR band and intensity of the semiconductor can be easily controlled via adjusting the stoichiometric ratios, vacancy, or dopant concentrations, as well as phase structures.[21–23] Among the plasmonic semiconductor nanostructures, tungsten oxide NWs, W₁₈O₄₉, made via a facile solvothermal method, possess intense LSPR band across the visible and NIR regions due to abundant oxygen vacancies on their surface. Such a broad plasmonic absorption in the NIR regions due to abundant oxygen vacancies on their surface.

Considering the comprehensiveness of the upconversion luminescence phenomenon, an enhanced catalytic activity for potential applications for the development of sustainable energy sources.

For the first time, we demonstrate the nonmetallic plasmonic-induced selective enhancement of upconversion luminescence in a layer-structured film consisting of NaYF₄:Yb-Er NPs as the upconversion layer and W₁₈O₄₉ NWs as the plasmonic layer. Compared with the individual NaYF₄:Yb-Er film, the NaYF₄:Yb-Er/W₁₈O₄₉ film exhibited a higher catalytic performance for the H₂ evolution from ammonia borane (BH₃NH₃).[27] Combining plasmonic W₁₈O₄₉ NWs with NaYF₄:Yb-Er NPs to form a hierarchical heterostructure would also promote the catalytic activity for the H₂ evolution due to the LSPR-induced interaction between both nanomaterials. This may reveal a new way to explore the NIR-active catalyst for potential applications for the development of sustainable energy sources.

![Diagram](https://www.advancedscience.com/fig1.png)

**Scheme 1.** Schematic diagram of plasmonic energy upconversion in the NaYF₄:Yb-Er NPs/W₁₈O₄₉ NWs system upon irradiation at 980 nm.

The enhanced upconversion luminescence of NaYF₄:Yb-Er NPs@W₁₈O₄₉ NWs quasi-core/shell structure synthesized via facile solvothermal method. To clarify the influence of W₁₈O₄₉ LSPR on the upconversion behavior of NaYF₄:Yb-Er NPs, a binary film with layer-on-layer heterostructure was designed and constructed hierarchically onto F-doped SnO₂ (FTO) glass. The FTO glass is chosen as the film substrate, because it contains abundant active sites for benefitting the uniform growth of plasmonic W₁₈O₄₉ NWs on its surface. Figure 1a shows the schematic illustration of the two-step assembly route and the profile of the NaYF₄:Yb-Er/W₁₈O₄₉ film. During the first step, W₁₈O₄₉ NWs were grown onto the FTO glass to achieve the plasmonic layer via a solvothermal process; for the second step, the NaYF₄:Yb-Er NPs were self-assembled on the top surface of the W₁₈O₄₉ NWs layer through a solvent evaporation process, therefore forming a thin upconversion-luminescence layer above the plasmonic layer. Meanwhile, two control samples were constructed on the FTO glass: one is the NaYF₄:Yb-Er film, which was fabricated by direct self-assembly of NaYF₄:Yb-Er NPs onto the FTO glass; the other is the NaYF₄:Yb-Er/N-W₁₈O₄₉ film, where the N-W₁₈O₄₉ NWs, denoting non-plasmonic W₁₈O₄₉ NWs, were obtained through the H₂O₂ treatment of plasmonic W₁₈O₄₉ NWs to passivate their surface oxygen vacancies.

The X-ray diffraction (XRD) pattern of the NaYF₄:Yb-Er/W₁₈O₄₉ film shows three sets of characteristic peaks, belonging to hexagonal β-NaYF₄, monoclinic W₁₈O₄₉, and tetragonal SnO₂, respectively (Figure 1b). Scanning electron microscopic (SEM) images display both top surface (Figure 1c) and cross section (Figure 1d) of the above film. It can be seen that NaYF₄:Yb-Er NPs with a mean size of ~40 nm are interconnected and cover the top surface of the composite film, thus forming a thin upconversion-luminescence layer. Furthermore, W₁₈O₄₉ NWs with diameters of 20–40 nm and lengths of 0.5–1.0 µm aligned in random orientations on the FTO glass, where they interweaved to compose a plasmonic layer (of ~500 nm...
thickness) below the upconversion-luminescence layer. The randomly tilted growth of W$_{18}$O$_{49}$ NWs on the film enabled the majority of self-assembled NaYF$_4$:Yb-Er NPs to directly contact the side surface of plasmonic W$_{18}$O$_{49}$ NWs. The control sample of NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$ film was identical to the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film in structural features and component morphology. Furthermore, the NaYF$_4$:Yb-Er film possessed similar thickness as the upconversion luminescence layer in the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film (Figure S1, Supporting Information). Figure 1e presents the comparison transmittance spectra of 1) W$_{18}$O$_{49}$ NWs, 2) N-W$_{18}$O$_{49}$ NWs, 3) NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$, and 4) NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ films. f) Upconversion emission spectra of 1) NaYF$_4$:Yb-Er, 2) NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$, and 3) NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ films. The insets provide the corresponding micro-area optical images achieved under irradiation at 980 nm. g) Histogram of enhancement factors calculated via the luminescence intensity ratios of NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film to the NaYF$_4$:Yb-Er film at the different emission wavelengths.

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Figure 1. a) Fabrication processes of the NaYF$_4$:Yb-Er, NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$, and NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$ films on FTO glass. b) XRD pattern of the as-fabricated NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film. SEM images of c) the top view and d) the side view of the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film. e) Transmittance spectra of 1) W$_{18}$O$_{49}$ NWs, 2) N-W$_{18}$O$_{49}$ NWs, 3) NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$, and 4) NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ films. f) Upconversion emission spectra of 1) NaYF$_4$:Yb-Er, 2) NaYF$_4$:Yb-Er/N-W$_{18}$O$_{49}$, and 3) NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ films. The insets provide the corresponding micro-area optical images achieved under irradiation at 980 nm. g) Histogram of enhancement factors calculated via the luminescence intensity ratios of NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film to the NaYF$_4$:Yb-Er film at the different emission wavelengths.
However, the NaYF4:Yb-Er/N-W18O49 film did not show the plasmonic absorption band in the visible–NIR region even though it shared the same component morphology with the NaYF4:Yb-Er/W18O49 film. Upconversion-luminescence properties of the as-fabricated films were tested via an inverted microscope coupled with a spectrometer and a 980 nm laser diode (Scheme S2, Supporting Information). It is clear that two green emission peaks and one red emission peak appearing on the spectrum of the NaYF4:Yb-Er film (Figure 1f) are attributed to $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$, $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$, and $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$ transitions of Er$^{3+}$ ions, respectively.[7–9] Also note that the intensity ratio of green-to-red emission ($I_{\text{green}}/I_{\text{red}}$) is only $\approx 1.4$, resulting in an overall green-yellow color output (see inset of Figure 1f). In the case of the NaYF4:Yb-Er/N-W18O49 film without plasmonic absorption property, the ratio value of $I_{\text{green}}/I_{\text{red}}$ is $\approx 1.7$, with the emission peak profiles almost identical to the corresponding parameters within the NaYF4:Yb-Er only film. This implies that the upconversion behavior of NaYF4:Yb-Er NPs is not influenced by the N-W18O49 NWs layer in the composite film. To our surprise, when these N-W18O49 NWs are replaced with the plasmonic W18O49 NWs in the composite film, the NaYF4:Yb-Er/W18O49 film exhibits a remarkable enhancement in the intensity for green emission; in particular, the emission peak at 521 nm was nearly one order of magnitude (9.0×) higher than the corresponding emission intensity of the NaYF4:Yb-Er film (Figure 1g). However, the red emission at 660 nm decreased to 10% of the NaYF4:Yb-Er film. As a result, the $I_{\text{green}}/I_{\text{red}}$ value of NaYF4:Yb-Er NPs increased to $\approx 75$ after introducing the plasmonic W18O49 NWs layer into the composite film. Thus, a bright green emission became noticeable on the micro-area photograph of the NaYF4:Yb-Er/W18O49 film in response to excitation with 980 nm (see inset of Figure 1f). It is apparent that a selective enhancement of green upconversion emission was found on the NaYF4:Yb-Er/W18O49 film.

When the NaYF4:Yb-Er NPs were deposited on the plasmonic W18O49 NW surface in the composite film, a strong interaction between LSPR and upconversion optical field occurred at their interface since the LSPR band of W18O49 NWs overlapped with both the excitation and emission electric fields of NaYF4:Yb-Er NPs (see Figure 1e). Upon 980 nm excitation, the W18O49 NWs serve as the “plasmonic antenna” to locally concentrate the NIR energy near the NWs, and then resonantly transfer this energy to adjoining NaYF4:Yb-Er NPs (Figure 2a).[28,29] Therefore, the NaYF4:Yb-Er NPs near the NaYF4:Yb-Er/W18O49 interface would experience a far more intense excitation electric field based on the surface enhancement effect, which could promote electron

**Figure 2.** a) Schematic diagram of the interaction between the LSPR effect of W18O49 NWs and the energy-transfer upconversion process of NaYF4:Yb-Er NPs. b) Simulated enhancements of excitation (980 nm) and emission electric-field intensities (521, 545, and 660 nm) at the plasmonic “hot spots” as a function of the contact positions between the NaYF4 NPs and W18O49 NWs. Insets show the simulation model of the NaYF4/W18O49 heterostructure with the NaYF4 NPs loaded on the representative positions of the W18O49 NWs surface; and the simulation of excitation electric field distribution at position P1 with input irradiation along the y-axis.
population on the excited-state energy levels of Er$^{3+}$ ions, thus resulting in an enhanced upconversion luminescence.$^{[6,7,10]}$

Meanwhile, the LSPR-enhanced localized electric field can interact with the emission electric field of NaYF$_4$:Yb-Er NPs to boost the radiative decay rate of upconversion process.$^{[4,7]}$

However, the direct contact of W$_{18}$O$_{49}$ NWs and NaYF$_4$:Yb-Er NPs quenches the upconversion emission to a certain degree due to the nonradiative energy transfer from the NaYF$_4$:Yb-Er NPs (donor) and the adherent W$_{18}$O$_{49}$ NWs (acceptor)$^{[31–34]}$

Moreover, the upconversion luminescence of NaYF$_4$:Yb-Er NPs can also be absorbed by the adjacent W$_{18}$O$_{49}$ NWs, which selectively weakens the luminescence intensity depending on the absorption band of W$_{18}$O$_{49}$ NWs. Furthermore, the LSPR-induced photothermal effect of W$_{18}$O$_{49}$ NWs can also raise the local temperature of NaYF$_4$:Yb-Er NPs to affect their upconversion process. Based on the above considerations, we proposed that the photophysical mechanism (Figure 2a) for this selective enhancement of upconversion luminescence is attributed to the following three aspects:

1) Plasmon-mediated competition between the radiative and nonradiative processes: We employed the finite element method to simulate the localized electric field intensity and distribution near the NaYF$_4$:Yb-Er NPs by plasmon-excitation of W$_{18}$O$_{49}$ NWs. The transmission electron microscopy (TEM) image suggests that the W$_{18}$O$_{49}$ NWs have a bundle-like nanostructure, consisting of several ultrathin secondary NWs with diameters of $\approx$10 nm (Figure S2a, Supporting Information). The TEM image of the NaYF$_4$:Yb-Er NPs confirmed their hexagonal nanostructure with a mean size of $\approx$40 nm (Figure S2b, Supporting Information). To simplify the calculation, a binary heterostructure is proposed in the simulation model, in which the single NaYF$_4$ NP is selectively loaded on the four representative positions of the bundle-like W$_{18}$O$_{49}$ NWs surface. As illustrated in the inset of Figure 2b, P1 and P2 represent the positions at the quarter and the half of W$_{18}$O$_{49}$ NWs, respectively, which are symmetric to the corresponding sites of P3 and P4. We first simulated the localized electric field distributions of the above four types of NaYF$_4$/W$_{18}$O$_{49}$ heterostructures under excitation of 980 nm. When the NaYF$_4$ NP was tangential to one of the NWs at P1 or P2 on the W$_{18}$O$_{49}$ bundle surface, the maximum electric field intensity enhancement ($\rho^2|E_p^2|$) could reach $\approx$29 at the plasmonic “hot spots,” i.e., in the vicinity of the NaYF$_4$/W$_{18}$O$_{49}$ interface (Figure 2b; Figure S2c, Supporting Information). Furthermore, if the NaYF$_4$ NP was deposited on either P3 or P4 to tangent simultaneously two of the NWs in the W$_{18}$O$_{49}$ bundle, it can obtain a $\approx$14-fold increase of the excitation electric field intensity at the NaYF$_4$/W$_{18}$O$_{49}$ interface (Figure S2c, Supporting Information). Interestingly, the distal edges of NaYF$_4$ NPs, opposite from the plasmonic “hot spots,” also showed a two- to four-fold enhancement of the localized electric field. Also note that the LSPR-enhanced excitation field concentrates mainly on the NaYF$_4$/W$_{18}$O$_{49}$ interface with a depth below $\approx$10 nm towards the NaYF$_4$. Second, interactions of W$_{18}$O$_{49}$ LSPR with the emission electric field of NaYF$_4$ NP were assessed through simulating the electric field distributions with emission wavelengths at 521, 545, and 660 nm, respectively (Figures S3–S5, Supporting Information). The maximum enhancement on the emission electric field intensities of the heterostructures also occurs near the NaYF$_4$/W$_{18}$O$_{49}$ interface. Moreover, the enhancement factors at different emission wavelengths fluctuate in a range from 3.4 to 8.0, depending on the contact sites of NaYF$_4$ NPs on the W$_{18}$O$_{49}$ NWs surface. It should be also noted that the emission electric field enhancement tendency and distributions close to the NaYF$_4$ NPs almost overlapped with the corresponding features of the excitation electric field enhancement induced by the W$_{18}$O$_{49}$ LSPR. As such, the overall enhancement of optical field at plasmonic “hot spots” of the NaYF$_4$/W$_{18}$O$_{49}$ heterostructures ranged from 70 to 220 times (Figure S6, Supporting Information).

However, in our case, the NaYF$_4$ NPs are directly in contact with the plasmonic W$_{18}$O$_{49}$ NWs and the nonradiative energy transfer to W$_{18}$O$_{49}$ NWs provides an efficient decay channel to quench the upconversion luminescence.$^{[31–34]}$ The time-resolved luminescence spectroscopy indicated that the lifetimes of $^4I_{11/2}$ $\rightarrow$ $^4I_{15/2}$ (521 nm), $^4I_{11/2}$ $\rightarrow$ $^4I_{15/2}$ (545 nm), and $^4I_{15/2}$ $\rightarrow$ $^4I_{15/2}$ (660 nm) decays for the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film were shorter than the corresponding lifetimes obtained from the individual NaYF$_4$:Yb-Er film (Figure S7, Supporting Information). Combining with the results of selective luminescence enhancement, we confirmed the existence of plasmon-mediated competition between the radiative and nonradiative processes in the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film after 980 nm excitation.$^{[6,7]}$ The radiative rate enhancement is originated from the plasmon-enhanced emission field, while the nonradiative process in the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film is mainly attributed to the mentioned energy transfer. This nonradiative energy transfer is strongly dependent on the distance between luminescent centers and plasmonic nanostructures.$^{[33,34]}$ For NaYF$_4$:Yb-Er NPs, the luminescent centers of Er$^{3+}$ ions are uniformly dispersed in the insulating NaYF$_4$ host.$^{[30]}$ Thus, the emission quenching process should occur only on the Er$^{3+}$ ions located near the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ interface. A large number of luminescent centers in the NaYF$_4$:Yb-Er NPs could enjoy the LSPR-enhanced excitation and emission fields with the weakened quenching effect, therefore leading to the enhancement of upconversion luminescence on the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film. To further confirm the existence of nonradiative energy transfer in the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film, we introduced the insulating spacer with different thicknesses to separate the NaYF$_4$:Yb-Er and W$_{18}$O$_{49}$ components, for the purpose of adjusting the energy transfer process (Figure S8, Supporting Information). Interestingly, when the thickness of the insulating spacer is proper, the upconversion luminescence of NaYF$_4$:Yb-Er NPs in the composite film could be further enhanced due to the suppressed nonradiative energy transfer (Figure S8, Supporting Information). Meanwhile, both the green and red emission enhancements were observed on the NaYF$_4$:Yb-Er/W$_{18}$O$_{49}$ film.

To gain a better understanding on the above plasmon-mediated competition process, we established the mathematical model based on a set of rate equations (Figure S9 and Equations (S1)–(S20), Supporting Information). The results demonstrated that the LSPR-enhanced excitation and emission fields were responsible for boosting the upconversion luminescence of
NaYF₄:Yb-Er NPs in the composite film. However, the transfer process of nonradiative energy competed against the LSPR-enhanced emission field to quench the upconversion luminescence. Importantly, we concluded that both the emission field enhancement and the nonradiative energy transfer contributed to the enlargement of intensity ratio between the green and red emissions, leading to a relatively strong green emission as compared to the light emission from the NaYF₄:Yb-Er/W₁₈O₄₉ film.

2) NIR-plasmonic energy upconversion: The LSPR-enhanced upconversion luminescence of NaYF₄:Yb-Er NPs can be partially absorbed by the adjacent W₁₈O₄₉ NWs due to their spectral overlap, which induces re-excitation of the LSPR effect of W₁₈O₄₉ NWs in the visible region, achieving an NIR-plasmonic energy upconversion process. According to the absorption spectrum of W₁₈O₄₉ NWs, the red emission from the NaYF₄:Yb-Er NPs should be more easily absorbed by the W₁₈O₄₉ NWs as compared to the emitted green light, which leads to a relatively strong green emission of NaYF₄:Yb-Er NPs on the W₁₈O₄₉ NWs film. When the W₁₈O₄₉ NWs layer did not possess the LSPR band in the visible region, both the green and red emission enhancements could be observed on the NaYF₄:Yb-Er/W₁₈O₄₉ film (Figure S9, Supporting Information). Thus, the NIR-plasmonic energy upconversion is one of the reasons for the selective absorption of upconversion luminescence.

3) Photothermal effect: After LSPR excitation by 980 nm, the W₁₈O₄₉ NWs can create a super-high temperature surrounding their surfaces (similar to the noble metal nanostructures), which would influence the upconversion luminescence of the neighboring NaYF₄:Yb-Er NPs in the composite film. It is well known that in the case of NaYF₄:Yb-Er, the energy separation (~840 cm⁻¹) between 2H₁₁/₂ and 4S₃/₂ levels can allow the thermally excited population from the 4S₃/₂ to 2H₁₁/₂ level, and a quasi-thermal equilibrium forms between these two levels, resulting in the variation in the transitions of 2H₁₁/₂ → 4I₁₅/₂ (521 nm) and 4S₃/₂ → 4I₁₅/₂ (545 nm) at an increased temperature (Equation (S21), Supporting Information). As observed in Figure 1f, the NaYF₄:Yb-Er/W₁₈O₄₉ film in our case shows a very large ratio of the green upconversion emissions from the 2H₁₁/₂ → 4I₁₅/₂ (521 nm) and 4S₃/₂ → 4I₁₅/₂ (545 nm) transitions, which suggests the high temperature located at the near-surface of NaYF₄:Yb-Er NPs due to the photothermal effect of W₁₈O₄₉ NWs.

Overall, this selective enhancement of upconversion luminescence over the NaYF₄:Yb-Er/W₁₈O₄₉ film was essentially caused by the plasmon-induced energy transfer between the plasmonic W₁₈O₄₉ NWs and NaYF₄:Yb-Er NPs (Figure 2a).

It is worth noting that the LSPR-enhanced near-filed effect mainly occurred at the very near region of the NaYF₄/W₁₈O₄₉ interface, which accounts for a small part of the luminescent centers in the NaYF₄ NP. Certainly, if the size of NaYF₄ NP reduces to allow more luminescent centers to locate in the plasmonic field, a more effective enhancement of upconversion luminescence is expected on the NaYF₄/W₁₈O₄₉ film. As we reduced the grain sizes of NaYF₄:Yb-Er NPs in the NaYF₄/W₁₈O₄₉ film, the enhancement factor of upconversion luminescence increased dramatically (Figure 3a; Figure S11, Supporting Information). Grain size reduction ensured that the major part of luminescent centers in the NaYF₄ NP was positioned within the effective interaction distance to enjoy the LSPR-enhanced field, leading to improved enhancement effect on the upconversion luminescence. Further investigation found that the enhancement factors of 4I₁₁/₂ → 4I₁₅/₂ transitions for all the samples were higher than those of 4S₃/₂ → 4I₁₅/₂ transitions. It reveals that the selective enhancement of upconversion luminescence of NaYF₄ NPs is due to the LSPR of W₁₈O₄₉ NWs in their composite film. Meanwhile, the optimal enhancement factor of 112× was achieved on the 10 nm NaYF₄:Yb-Er NPs (Figure 3a). Although 10 nm NaYF₄:Yb-Er NPs exhibited optimal enhancement effect in our study, 40 nm NaYF₄:Yb-Er NPs showed the largest luminescence intensity after plasmonic sensitization via W₁₈O₄₉ NWs (Figure 3b).

Plasmonic W₁₈O₄₉ NWs are an effective catalyst for boosting the H₂ release from BH₃NH₃ via catalytic hydrolysis. Coupling plasmonic W₁₈O₄₉ NWs with Ln³⁺-doped NaYF₄ NPs to construct a hierarchical heterostructure would result in a highly efficient H₂ evolution due to the NIR-plasmonic energy upconversion process. Considering that the catalytic active sites locate on the W₁₈O₄₉ NWs surface, a quasi-core/shell heterostructured catalyst was designed and synthesized via solvothermal growth of W₁₈O₄₉ NWs onto hydrophilic NaYF₄:Yb-Er NPs with a grain size reduction, leading to improved catalytic performance. Figure S12 shows the TEM images of the NaYF₄:Yb-Er/W₁₈O₄₉ catalysts with different grain sizes.

Figure 3. a) Luminescence enhancement factor of 2H₁₁/₂ and 4S₃/₂ to 4I₁₅/₂ transitions as a function of the grain sizes of NaYF₄:Yb-Er NPs; b) micro-area optical images of the as-fabricated films loaded with different sizes of upconversion NPs under irradiation at 980 nm: 1) NaYF₄:Yb-Er films; 2) NaYF₄:Yb-Er/W₁₈O₄₉ films.
size of ≈40 nm (Figure 4a). The as-synthesized NaYF₄:Yb-Er@W₁₈O₄₉ nanocomposite possesses a spherical structure that exposes numerous NWs on the surface, thus forming a “sea urchin-like” catalyst (Figure 4b). The diameters of the NaYF₄:Yb-Er@W₁₈O₄₉ heterostructures were around 1 μm. The TEM image shows that the NWs on the heterostructure surface are 400–600 nm in length and 10–30 nm in diameter. The TEM elemental mapping of an individual NaYF₄:Yb-Er@W₁₈O₄₉ heterostructure presents that the Na, Y, and F elements are mostly distributed in the center of the heterostructure, while the W and O elements are present throughout the whole profile, indicating the formation of the quasi-core/shell heterostructure (Figure 4c). The characterization results of the selected area electron diffraction (SAED) and XRD patterns unambiguously confirm that the as-synthesized heterostructures consisted of the cubic α-NaYF₄ and the monoclinic W₁₈O₄₉ (Figure 4d,e).

Notably, the NaYF₄:Yb-Er@W₁₈O₄₉ heterostructure still displayed an intense LSPR absorption band that overlaps with both the excitation and emission spectra of the NaYF₄:Nd Er NPs (Figure 4f). Taking this LSPR feature, the NaYF₄:Yb-Er@W₁₈O₄₉ heterostructures also exhibited selectively enhanced upconversion emission, as deduced from the normalized emission spectra (Figure 4g). This suggests that the as-proposed NIR-plasmonic energy upconversion process occurs in the NaYF₄:Yb-Er@W₁₈O₄₉ heterostructure, which could offer a new and efficient way to enhance the catalytic H₂ evolution from BH₃NH₃.

The catalytic activity of the as-synthesized NaYF₄:Yb-Er@W₁₈O₄₉ heterostructure was evaluated via hydrolysis of BH₃NH₃ under irradiation of 980 nm laser diode with a spot area of ≈0.5 cm². As shown in Figure 5a, in the absence of catalysts, a very low H₂ evolution happened after 1 h of 980 nm irradiation (≈0.06 μmol), suggesting a slow hydrolysis process of BH₃NH₃. When adding W₁₈O₄₉ NWs into the reaction solution without light irradiation, a slight increase in the H₂ evolution (≈0.12 μmol) could be observed (Figure S12, Supporting Information), demonstrating the poor catalytic activity of unexcited plasmonic W₁₈O₄₉ NWs. However, upon 980 nm irradiation, the H₂ evolution amount was substantially increased to ≈0.60 μmol after 1 h. The pure NaYF₄:Yb-Er NPs
showed a negligible H2 generation (Figure S12, Supporting Information). These results revealed that the excited LSPR of W18O49 NWs could greatly boost the catalytic H2 evolution due to the plasmonic transfer process of “hot electrons,” as outlined in previous publications.[21,27] Importantly, the H2 evolution amount of the NaYF4:Yb-Er@W18O49 heterostructure can reach ≈2.11 µmol with the apparent quantum efficiency of ≈2.8% under 1 h irradiation of 980 nm (Equation (S22), Supporting Information). This H2 evolution amount is about 3.5 times higher than the H2 evolution of pure W18O49 NWs and even 35 times higher than the H2 evolution of single BH3NH3 hydrolysis. Meanwhile, the apparent quantum efficiency is comparable to the corresponding values obtained in other visible-light photocatalysts. [40–42] This implies that the upconversion NPs play a central role on the enhanced catalytic activity of the H2 evolution. Namely, the upconversion emission of Ln3+-doped NaYF4 NPs at a suitable wavelength region can improve the LSPR excitation of the W18O49 NWs and enhance the catalytic activity for H2 evolution on the surface of W18O49 NWs. This hypothesis can be verified via wavelength-dependent H2 evolution plots of W18O49 NWs. As shown in Figure 5b, the H2 evolution amount of W18O49 NWs is directly correlated with the photon energy that can be absorbed by the W18O49 NWs to drive the LSPR effect.[21,24,27,38] It is apparent that the LSPR band of W18O49 NWs overlapped with the green and red emissions of the NaYF4:Yb-Er NPs. As a result of this, the enhanced catalytic activity of the NaYF4@W18O49 heterostructures can be attributed to the NIR-plasmonic energy upconversion induced by the LSPR effect of W18O49 NWs.

If this were true, the catalytic enhancement factor should be related to the excitation power density of the incident light.[41,44] As shown in Figure 5c, the H2 evolution amounts of both the W18O49 NWs and NaYF4:Yb-Er@W18O49 heterostructures depended strongly on the power density of 980 nm laser diode. Furthermore, the enhancement factor gradually increased with the power density of incident light (Figure 5d). Therefore, it can be concluded that the light intensity illuminated on W18O49 dominated the enhanced catalytic activity. Besides, the NaYF4@W18O49 heterostructure was also a reusable plasmonic catalyst (Figure S13, Supporting Information). Furthermore, the catalytic activity of NaYF4:Yb-Er@W18O49 heterostructures for H2 evolution increases with the size of NaYF4:Yb-Er hetero-component (Figure S14, Supporting Information). Also note that a NaYF4:Yb-Er/W18O49 film with the larger sizes of NaYF4:Yb-Er NPs exhibited a higher intensity of upconversion luminescence, but a smaller enhancement factor. Thus, coupling plasmonic W18O49 NWs with the larger sizes of NaYF4:Yb-Er NPs in their heterostructure could lead to a more efficient NIR-plasmonic energy upconversion to excite the LSPR of W18O49 NWs for catalytic H2 evolution.

In summary, we have demonstrated the selective enhancement of upconversion luminescence behavior on the well-designed heterostructure film fabricated via self-assembly of NaYF4:Yb-Er NPs onto the nonmetallic plasmonic layer of
W18O49 NWs grown on an FTO glass substrate. Investigations showed that the broad LSPR absorption band of W18O49 NWs overlapped with both the excitation and emission bands of NaYF4:Yb-Er NPs, which could induce an NIR-plasmonic energy upconversion process, thus resulting in 9- to 112-fold enhancement of green emission on the NaYF4:Yb-Er/W18O49 film as compared to the pure NaYF4:Yb-Er NP film. By using this fascinating photophysical process, we also realized a promoted catalytic activity for H2 evolution from BH3NH3 over the quasi-core/shell heterostructure was 35 times higher than that of BH3NH3 only developed feasible and low-cost tactics to selectively enhance the upconversion luminescence of Ln3+-doped NaYF4 NPs, but also offered a new class of NIR-responsive heterostructure catalysts that possess an efficient catalytic activity for H2 evolution based on the NIR-plasmonic energy upconversion process.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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