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An Optical Probe Possessing Upconversion Luminescence and Hg²⁺-Sensing Properties

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A Hg²⁺-selective chromophoric upconversion nanosystem is achieved by covalently grafting Rhodamine B hydrazide (RB-hydrazide) onto upconversion luminescent nanorod core-shell structures. The prepared β -NaYF₄ nanorods are coated with silica and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), Fourier-transform infrared spectroscopy (FTIR), and photoluminescence

spectra. Under 980 nm excitation, the upconversion luminescence is sensitive towards Hg²⁺ because RB-hydrazide-Hg can efficiently absorb green upconversion emission. The prepared nanocomposites exhibit high sensitivity and selectivity towards Hg²⁺ over other metal ions. These results indicate that this nanosystem could be developed as a promising fluorescence probe for detecting Hg²⁺ ions.

1. Introduction

Mercury is one of the most toxic and dangerous heavy metal elements because of its high affinity for thiol groups in proteins and enzymes, leading to dysfunction of cells and consequently many health problems in brain, kidney, central nervous and endocrine systems.^[1] Therefore, the detection and quantification of Hg²⁺ in environmental monitoring are of importance.

Fluorescent chemodosimeters have become a powerful tool for sensing trace amounts of Hg²⁺ owing to their simplicity, short responsive time, high sensitivity and selectivity.^[2] To date, some of them have been successfully applied in fluorescent imaging of Hg²⁺ in biosamples.^[2 g-2n] However, these probes need photoexcitation in UV/visible light region, in which the endogenous chromophores or acceptors can also be excited, leading to background light interference and thus limiting their applications in biological systems. The use of lanthanide-doped upconversion nanomaterials, which convert near-infrared (NIR) to visible light,^[3] provides an alternative method for Hg²⁺ monitoring. Recently, there is an increasing interest in sensing and bioimaging based on NIR to visible upconversion materials as luminescent labels.^[4] Compared with down-con-

version fluorescent materials such as organic dyes and quantum dots, upconversion materials own many advantages including large Stokes shifts, higher chemical stability, reinforced light penetration depth in tissue, lower toxicity and negligible levels of autofluorescence.^[5] Wolfbeis and co-workers have developed a series of upconversion luminescence-based chemosensors in sensing pH, NH₃ and O₂.^[6] A later work by Li et al. developed ruthenium or iridium complex-coated nanosystems for sensing and bioimaging of Hg²⁺ or CN⁻.^[7]

Among the reported upconversion materials, NaYF₄ lattice has been widely recognized as one of the most efficient hosts for upconversion rare earth ions.^[8] However, most of upconversion NaYF₄ materials are synthesized in organic solvents^[9] or at high temperatures,^[10] the obtained nanocrystals are thus hydrophobic, showing poor dispersibility in water. Therefore, further surface modification of these nanocrystals is much required. Because of the well-known surface chemistry, benign effects on biological systems and the facile grafting with other functional groups,^[11] silica-coated core-shell structures are generally considered to be an ideal method for the modification of upconversion nanocrystal surfaces. Zhang and co-workers used silica-coated upconversion nanoparticles encapsulated with organic dyes or quantum dots for fluorescence resonance energy-transfer modulation of upconversion luminescence emission spectra.^[12] The obtained results show great promise for the design and application of multifunctional upconversion nanomaterials in analytical and biological fields.

In this paper, a highly sensitive probe for upconversion luminescence sensing of Hg²⁺ is achieved by covalently grafting RB-hydrazide onto silica-coated upconversion luminescent nanorods. This system is expected to be used for selective and sensitive quantification of Hg²⁺ in environmental and biological monitoring.

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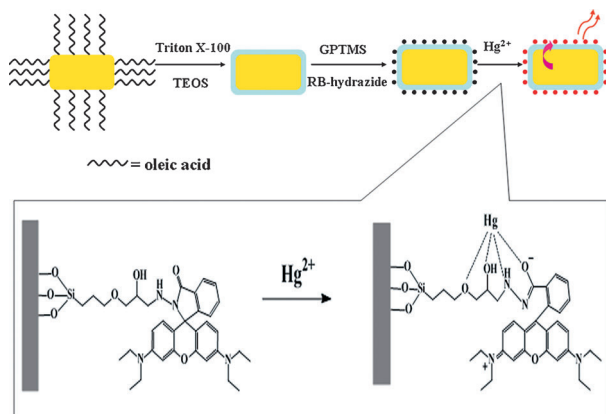
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2. Results and Discussion

2.1. Characterization of Upconversion Nanorods

The synthetic strategy is shown in Scheme 1. Our design strategy for the Hg^{2+} -selective chromophoric upconversion nanosystem is based on the Hg^{2+} modulating energy transfer



Scheme 1. Schematic illustration of the synthesis of RB-hydrazide-modified $\beta\text{-NaYF}_4@SiO_2$ materials and their upconversion luminescence response to Hg^{2+} .

degree from upconversion luminescence emission of $\beta\text{-NaYF}_4$ nanorods to the absorbance of RB-hydrazide-Hg. Here, a facile and user-friendly method was developed to synthesize core-shell-structured $\beta\text{-NaYF}_4@SiO_2$ by surfactant-assisted sol-gel coating. Uniform $\beta\text{-NaYF}_4$ -codoped Yb^{3+} and Er^{3+} nanorods were prepared by a hydrothermal method reported in the literature.^[9a] Oleic acid was used as a stabilizing agent, while $\text{Ln}(\text{NO}_3)_3$ and NaF were used as precursors at 200°C . A high F^- concentration was used in favor of the dissolution–reconstruction process, which caused a fast crystal growth along the [0001] direction and ultimately formed the nanorods.^[9a] The XRD pattern (Figure 1) of the as-made sample agrees well with

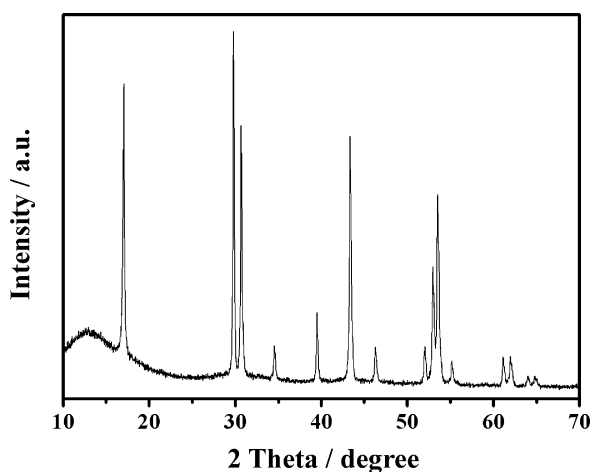


Figure 1. XRD pattern of the as-prepared $\beta\text{-NaYF}_4$ nanorods.

that of pure hexagonal NaYF_4 nanocrystals, as reported in the Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 16-0334). No other phase is detected, revealing that Yb^{3+} and Er^{3+} have been successfully doped into the host lattices of $\beta\text{-NaYF}_4$. The SEM images show that the nanorods are uniform, with diameter of about 150 nm and length of about 1.7 μm (Figure 2a). It can be seen from the inset of Figure 2a that

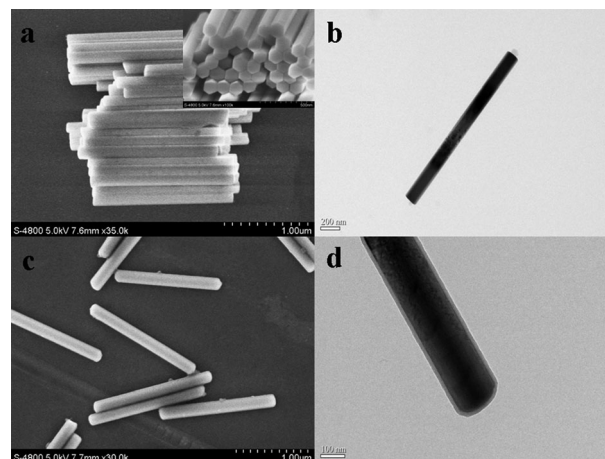


Figure 2. SEM and TEM images of a,b) $\beta\text{-NaYF}_4$ nanorods and c,d) silica-coated $\beta\text{-NaYF}_4@SiO_2$.

both top and bottom ends of these nanorods are hexagonal. The TEM image (Figure 2b) further indicates the nanorods with smooth surface. These results show that pure hexagonal $\beta\text{-NaYF}_4$ nanorods with good uniformity and smooth surface are obtained under the present experimental conditions.

As mentioned above, hydrophobic oleic acid ligands are modified with the amphiphilic nonionic surfactant Triton X-100 to obtain a hydrophilic surface. The hydrophobic segment of Triton X-100 can interact with the alkyl chains of oleic acid, which are located outside the surface of the nanorods, so that the hydrophilic group is dispersed on the external surface. Therefore, after modification, the surface of the $\beta\text{-NaYF}_4$ nanorods changes to hydrophilic, and can be directly coated with a silica layer by using the mature Stober sol-gel method. The SEM image is shown in Figure 2c. It is observed that all nanorods have been successfully coated, with no silica nanoparticles. The TEM image in Figure 2d shows that the thickness of the silica shell is as thin as 10 nm. The EDAX pattern (see Figure S1 in the Supporting Information) further confirms that the nanorods are coated by a silica layer. The XRD pattern of $\beta\text{-NaYF}_4@SiO_2$ shows well-resolved diffraction peaks similar to those of their parent $\beta\text{-NaYF}_4$ nanorods, proving that the hexagonal crystalline phase is well retained (see Figure S2 in the Supporting Information).

The presence of RB-hydrazide covalently bonded onto the silica shell can be further confirmed by FTIR spectra. As for the $\beta\text{-NaYF}_4@SiO_2$ nanorods modified with epoxy silicon (Figure 3A), the formation of a Si–O–Si framework is evidenced by the absorption bands of the siloxane bond, located at 1080 cm^{-1} (ν_{asr} Si–O), 803 cm^{-1} (ν_{sr} Si–O) and 462 cm^{-1} (δ , Si–

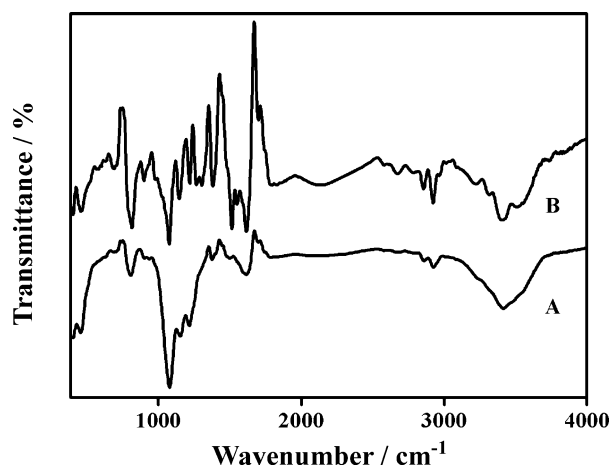


Figure 3. FTIR spectra of β - NaYF_4 @ SiO_2 nanorod epoxy silicon (A) and RB-hydrazide-modified β - NaYF_4 @ SiO_2 nanocomposites (B).

O–Si), respectively (ν represents stretching, δ in-plane bending, s symmetric, and as asymmetric vibrations). Furthermore, the band at 1382 cm^{-1} can be assigned to the stretching vibration of the $-\text{C}-\text{O}-\text{C}-$ group, indicating the presence of epoxy silicon on the surface of the β - NaYF_4 @ SiO_2 nanorods. The new peak at 1515 cm^{-1} in Figure 3B is attributed to the bending vibration of δ N-H, proving that RB-hydrazide has been successfully covalently bonded onto the silica framework.

2.2. Sensing Performance of β - NaYF_4 @ SiO_2 -Rodamine B toward Hg^{2+}

The sensing ability of β - NaYF_4 @ SiO_2 -Rhodamine B (RB) for Hg^{2+} was investigated by spectral overlap and upconversion luminescence spectra. Figure 4 shows that upon excitation with a 980 nm laser, the upconversion nanorods display green and red emission bands peaking at 521, 539, and 651 nm, which can be assigned to ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$

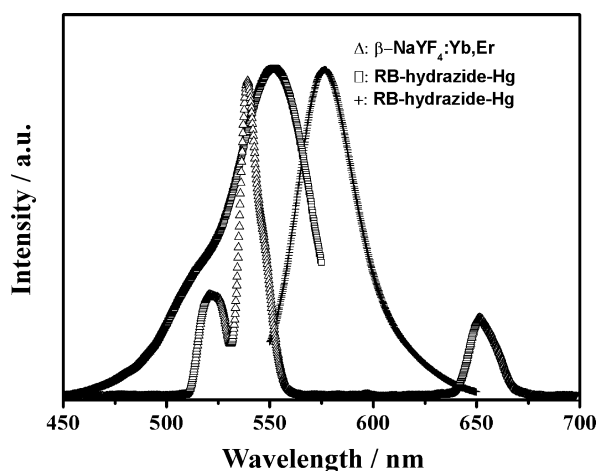


Figure 4. Excitation (\square) and emission ($+$) spectra of RB-hydrazide-modified β - NaYF_4 @ SiO_2 in the presence of Hg^{2+} ($2\text{ }\mu\text{M}$), and upconversion luminescence emission of β - NaYF_4 :Yb, Er nanorods (\triangle) under 980 nm excitation.

transitions of Er^{3+} , respectively (see Figure S3 in the Supporting Information). The free RB-hydrazide of spirolactam structure is nearly non-fluorescent. However, in the presence of Hg^{2+} , a delocalized xanthene moiety of the RB group can be generated, resulting in a strong fluorescence emission.^[13] It can be seen from Figure 4 that: 1) the green upconversion luminescence overlaps perfectly with excitation spectrum of β - NaYF_4 @ SiO_2 -RB in the presence of Hg^{2+} , indicating the possibility that RB-hydrazide-Hg can absorb green light from upconversion nanorods; 2) their emission spectra are quite different in wavelength and band width, making it possible to compare the two spectra and consequently evaluate the emission/reabsorption process; and 3) the upconversion nanorods can be excited by a NIR laser at 980 nm where RB-hydrazide-Hg cannot be photoexcited, thereby completely avoiding direct excitation of RB-hydrazide-Hg by external light and eliminating luminescence background interference.

Importantly, as shown in Figure 5, upon increasing concentrations of Hg^{2+} , the intensity of green emissions at 521 and 539 nm decreases gradually. On the other hand, the red emis-

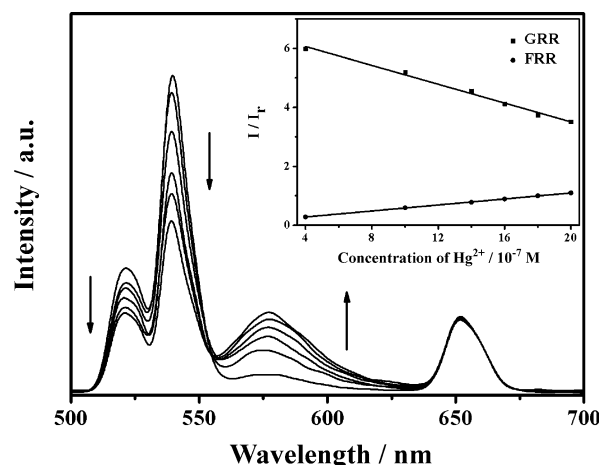


Figure 5. Upconversion luminescence spectra of β - NaYF_4 @ SiO_2 -RB in aqueous solutions with increasing Hg^{2+} concentrations. Inset: variations of both green-to-red emission ratio (GRR) of Er^{3+} and fluorescence emission to red emission ratio (FRR) of RB-hydrazide-Hg at different concentrations of Hg^{2+} .

sion at 651 nm is not affected since RB-hydrazide-Hg has no absorption at 651 nm, the red emission intensity can thus serve as a reference. Simultaneously, a new peak centered at 580 nm, attributable to the characteristic emission of RB-hydrazide-Hg, appears, confirming that RB-hydrazide-Hg can efficiently absorb green erbium emission at 520–550 nm and emit its fluorescence. Correspondingly, the fluorescence emission intensity of RB-hydrazide-Hg has an obvious increase with the addition of Hg^{2+} . The inset of Figure 5 exhibits the variation of green (${}^2\text{H}_{11/2} + {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$) to red (${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) emission ratio (GRR) of Er^{3+} and fluorescence emission of RB-hydrazide-Hg to red (${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) emission ratio (FRR) at different concentrations of Hg^{2+} . It can be seen that the addition of Hg^{2+} causes a decreased GRR and an increased FRR, suggesting the emission/reabsorption from upconversion nanorods to

RB-hydrazide–Hg. Thereby, the system as a highly selective probe for upconversion luminescence sensing of Hg^{2+} is possible. The detection limit of $\beta\text{-NaYF}_4\text{@SiO}_2\text{-RB}$ for Hg^{2+} is calculated to be about 10^{-7} M in aqueous solution.^[14]

High selectivity is highly desired for excellent probes. In the present work, the optical response of $\beta\text{-NaYF}_4\text{@SiO}_2\text{-RB}$ is extended to other metal cations in aqueous solutions. Figure 6 il-

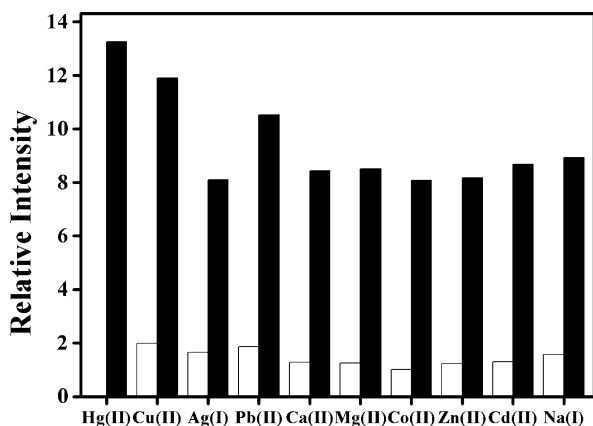


Figure 6. Upconversion fluorescence responses of $\beta\text{-NaYF}_4\text{@SiO}_2\text{-RB}$ to various cations in aqueous solution. The white bars represent the emission intensities of $\beta\text{-NaYF}_4\text{@SiO}_2\text{-RB}$ in the presence of various interfering ions (all at 10^{-3} M). The black bars represent the change of the emission that occurs upon subsequent addition of 10^{-6} M of Hg^{2+} to the above solution. $\lambda_{\text{ex}} = 980$ nm, $\lambda_{\text{em}} = 580$ nm.

lustrates the selectivity of $\beta\text{-NaYF}_4\text{@SiO}_2\text{-RB}$. No significant changes on fluorescence spectra are observed upon addition of other metal cations, such as Na^+ , Ag^+ , Pb^{2+} , Cu^{2+} , Mg^{2+} , Ca^{2+} , Co^{2+} , Cd^{2+} and Zn^{2+} . However, the addition of Hg^{2+} causes a prominent fluorescence enhancement, which is obviously different from the cases for other metal ions, indicating the high selectivity for Hg^{2+} . We attribute the special selectivity for Hg^{2+} to several combined influences, such as the suitable coordination geometry conformation of the receptor, the larger radius of Hg^{2+} ion, the nitrogen-affinity of Hg^{2+} ions, and the amide deprotonation ability of Hg^{2+} ion.^[15]

3. Conclusion

In summary, core/shell-structured $\beta\text{-NaYF}_4\text{@SiO}_2$ nanorods with very thin and uniform silica coatings have been prepared via the surfactant-assistant approach. Because of the upconversion luminescence nanorods core ($\beta\text{-NaYF}_4$) and fluorescent receptor (RB-hydrazide) immobilized onto silica shell by covalent bonding, the system exhibits a high selectivity for upconversion luminescence sensing of Hg^{2+} . Economical starting materials, straightforward synthetic strategy, NIR-to-vis upconversion luminescence and good selectivity for Hg^{2+} , endow the system with further potential applications for Hg^{2+} detection in biological and analytical fields.

Experimental Section

Materials

All chemicals involved in this work were of analytical grade and used without further purifications. Y_2O_3 , Yb_2O_3 and Er_2O_3 were purchased from Shanghai Chemical Industrial Co. All the rare earth nitrates were prepared by dissolving corresponding rare earth oxides in 20% nitric acid solution and then evaporating solvent water completely. Anhydrous ethanol, concentrated ammonia aqueous solution (28 wt%), oleic acid (90 wt%), tetraethoxysilane (TEOS), 3-glycidyloxypropyltrimethoxysilane, rhodamine B and hydrazine hydrate (85 wt%) were purchased from Shanghai Chemical Company (Shanghai, China). Triton X-100 (tert-octylphenoxypolyoxyethylene, Guangdong Chemicals Co.) and NaF (Tianjin Chemicals Co.) were used as received. NaOH and toluene were obtained from Beijing Chemicals Company (Beijing China). Deionized water was used in our present work.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer (Germany) with Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were taken with a JEM-2010 transmission electron microscope made by Japanese JEOL Company. All samples were firstly dispersed in ethanol and then collected using copper grids covered with carbon films for measurements. The energy-dispersive analysis of X-ray (EDAX) and scanning electronic microscopy (SEM) images were obtained on a Hitachi S-4800 microscope. Fourier-transform infrared (FT-IR) spectra were collected on a Nicolet Fourier spectrophotometer using KBr pellets. Optical measurements were acquired on a Hitachi F-4500 fluorescence spectrophotometer under the excitation of a 980 nm laser diode.

Synthesis of Upconversion Nanorods

The hexagonal phase $\beta\text{-NaYF}_4$ -codoped Yb^{3+} and Er^{3+} nanorods were prepared by a modified process of literature report.^[9a] A typical procedure can be described as follows: 0.7 g (17.5 mmol) of NaOH, 7.1 g (22.6 mmol) of oleic acid (90 wt%) and 10.0 g of ethanol were well mixed at room temperature to get a white viscous solution. 10.0 mL (8 mmol) of 0.8 M NaF solution was added under vigorous stirring until a translucent solution was obtained. Then, 2.0 mL (0.8 mmol) of 0.4 M $\text{Y}(\text{NO}_3)_3$, 1.0 mL (0.2 mmol) of 0.2 M $\text{Yb}(\text{NO}_3)_3$ and 2.0 mL (0.02 mmol) of 0.01 M $\text{Er}(\text{NO}_3)_3$ were poured into the above solution under vigorous stirring. After aging for 20 min, the mixing solution was transferred into a Teflon bottle held in a stainless-steel autoclave, sealed, and maintained at 200 °C for 24 h. As the autoclave was cooled to room temperature naturally, the precipitates were separated by centrifugation and then washed with ethanol and deionized water in sequence. The solid product was dried in air at 80 °C for 12 h.

Synthesis of $\beta\text{-NaYF}_4\text{@SiO}_2$ Core–Shell Nanorods

In a typical synthesis,^[16] 0.10 g of upconversion nanorods was added into 20 mL of Triton X-100 solution and treated with ultrasound for 10 min to form a transparent solution. Then, 80 mL of water was poured into above solution under continuous stirring for 6 h. After being centrifugated and washed with deionized water, the precipitation was dispersed in the mixture of ethanol (160 mL), deionized water (40 mL) and concentrated ammonia aqueous solution (2.0 mL, 28 wt%), then 0.06 g of TEOS was added. After stirring for another 6 h, the product was separated by

centrifugation, washed with ethanol and deionized water in sequence, and β -NaYF₄@SiO₂ nanorods were finally obtained.

Synthesis of β -NaYF₄@SiO₂ Nanorod Epoxy Silicon (β -NaYF₄@SiO₂-ES)

β -NaYF₄@SiO₂ (0.05 g) and 3-glycidyloxypropyltrimethoxysilane (0.05 mL) in anhydrous toluene (15 mL) were refluxed for 24 h under nitrogen atmosphere at 112 °C. The product was washed with toluene, and then dried under vacuum.

Synthesis of RB-Hydrazide-Functionalized β -NaYF₄@SiO₂ Nanocomposites (β -NaYF₄@SiO₂-RB)

RB-hydrazide was prepared according to a reported procedure.^[17] β -NaYF₄@SiO₂-ES (0.05 g) was allowed to react with RB-hydrazide (0.05 g) in anhydrous toluene (15 mL) under reflux under nitrogen atmosphere for 12 h. The product was washed with toluene, and then dried under vacuum.

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