Multifunctional Lanthanide-Doped Core/Shell Nanoparticles: Integration of Upconversion Luminescence, Temperature Sensing, and Photothermal Conversion Properties

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Supporting Information

ABSTRACT: Multifunctional integration on single upconversion nanoparticles (UCNPs), such as the simultaneous achievement of imaging, sensing, and therapy, will be extremely attractive in various application fields. Herein, we demonstrated that single core/shell NaGdF₄:Yb/Er-based UCNPs (<10 nm) with a highly Yb³⁺ or Nd³⁺ doped shell simultaneously exhibited good upconversion luminescence (UCL), temperature sensing, and photothermal conversion properties under 980 or 808 nm excitation, respectively. The spatial separation between the emission/sensing core and the heating shell was able to tailor the competition between the light and heat generation processes, and hence higher UCL efficiency and enhanced heating capability were achieved by introducing the rational core/shell design. Especially, Nd³⁺-sensitized core/shell nanoparticles were excitable to the laser at a more biocompatible wavelength of 808 nm, and hence the heating effect of water was greatly minimized. The heating and sensing capabilities of Nd³⁺-sensitized core/shell UCNPs with smaller sizes (<10 nm) were confirmed in aqueous environment under single 808 nm laser excitation, implying their promising applications in imaging-guided and temperature-monitored photothermal treatments.

INTRODUCTION

Upconversion nanoparticles (UCNPs) possess unique luminescence properties of emitting visible light under near-infrared (NIR) light excitation and therefore can be widely applied in various fields from bioprobing to photovoltaics. In comparison with traditional luminescent nanomaterials including organic dyes and quantum dots, UCNPs have numerous advantages for bioapplications, such as improved penetration depth, minimized autofluorescence, low radiation damage and cytotoxicity, high chemical and optical stability, etc. UCNPs also can act as an ideal multifunctional platform capable of simultaneous multimodality imaging or simultaneous imaging, detection, and therapy. Lin et al. synthesized NaYF₄:Yb/Tm@NaGdF₄:Yb core/shell nanoparticles, which could be used for X-ray computed tomography (CT), magnetic resonance imaging (MRI), and upconversion luminescence (UCL) trimodal imaging. Sun et al. designed multifunctional NaLaF₄:Yb/Tm@NaGdF₄:Sm core/shell UCNPs for four-modality imaging, including CT, MRI, UCL, and single-photon emission computed tomography imaging. The incorporation of UCNPs and mesoporous silica could combine diagnosing and treating capabilities within a single platform and achieve controlled drug delivery and multimodal imaging at the same time. Moreover, UCNPs could be coupled to magnetic, metal, or semiconductor nanostructures to construct multifunctional nanocomposites capable of utilizing their distinct properties or coupling effects.

The simultaneous achievement of a variety of functions on individual UCNPs would be highly desired for their applications. In UCNPs, such as intensively investigated hexagonal (β) phase NaYF₄:Yb/Er, only less than 1% of absorption energy is converted into upconversion emissions. Most of the absorption energy is released via downconversion luminescence or heat generation. In this regard, single UCNPs also can be considered for photothermal treatment applications if the heat generation is efficient enough. Photothermal nanomaterials are capable of precise and selective nanoscale heating, which can be widely applied to cancer treatments, data storage and microflow driving in microfluidic chips. In comparison with these photothermal nanomaterials, UCNPs exhibit unique advantages for practical applications. On the basis of their temperature-sensitive fluorescence, UCNPs demonstrate certain capability for nanoscale temperature sensing.
their particular upconversion emissions, UCNPs are able to simultaneously behave as optical nanoheaters, temperature nanosensors, and luminescent probes. The integration of temperature sensing and optical imaging functions on photothermal nanomaterials is very beneficial to photothermal therapy, allowing for dynamic control over treatment processes and parameters. Temperature reading by the heating nanoparticles during therapeutic processes will be of vital importance to minimize the collateral damage arising from undesirable overheating. The visible upconversion emissions are conducive to proper location of photothermal nanoparticles inside the targeted cells. In addition, on the basis of their inherent photothermal conversion capability, our group demonstrated that core/shell or composite UCNPs exhibited obvious UCL color shifts as exposed to a commercially available NIR laser, thus allowing for producing more secure anticounterfeiting patterns with simple authentication methods.30–32

As has been previously mentioned, multifunctional UCNPs with heating, sensing, and UCL properties exhibit potential applications in various fields. A few studies reported the photothermal conversion properties of lanthanide-doped fluoride nanoparticles.15,27–32 For example, Carrasco et al. synthesized highly Nd3+ doped LaF3 downconversion nanoparticles, and demonstrated the feasibility of their applications in temperature-controlled photothermal tumor treatments.27 Marciniak et al. designed NaNdF4@NaYF4@NaYF4:1%Nd3+ core/shell nanoparticles, which were capable of combining efficient photothermal conversion and highly sensitive temperature probing on single nanoparticles.28 In comparison with downconversion luminescence nanomaterials, UCNPs featured with NIR light excitation will be a more ideal choice for the multifunctional integration on individual nanoparticles. Our group demonstrated that NaGdF4:Yb/Er UCNPs with smaller sizes (<10 nm) simultaneously showed UCL, thermal sensing, and photothermal conversion properties.29–31 Suo et al. reported that YF3:Tm/Yb microcrystals showed great potential for applications as real-time thermal sensors and photothermal agents.32 It is noteworthy that high-power laser radiation has to be used for reaching the adequate temperature increase, and thus further improvements of the heating capability of UCNPs are necessary. The heat generation process directly competes with the luminescence process, and normally the heating capability is improved at the expense of the luminescence efficiency. The core/shell structural design provides an effective route to balance the competition between the heating and luminescence processes and thus offers the possibility of achieving enhanced photothermal conversion and high luminous efficiency at the same time. Tong et al. synthesized NaYF4:Sm/Yb@NaYF4:Er/Yb core/shell nanoparticles (>20 nm), in which the core and shell acted as the heating center and temperature sensing unit, respectively.33 However, the UCL efficiency of the outmost NaYF4:Er/Yb shell would be unavoidably affected by the surface quenching process. Ximendes et al. designed more interesting LaF3:Yb/Er@LaF3:Nd core/shell UCNPs (~30 nm), in which the shell behaved as the heating unit and the emission core provided the temperature sensing function.34 It is worth noting that these core/shell UCNPs showed larger particle sizes (>20 nm) that were not optimal for biological applications. UCNPs with smaller sizes and promising luminescence/sensing/heating properties will be highly desired in the biomedical field for the target of fast body clearance of nanoparticles and minimized interference with cellular systems.33 Although the integration of simultaneous heating and temperature sensing also can be achieved by coupling lanthanide-doped nanoparticles (as thermal sensors) with metal, magnetic, or carbon nanostructures (as heating units), these nanocomposites normally suffer from complicated nanostructures, tedious synthesis procedures, and larger sizes.9,10,34 The simultaneous achievement of UCL, thermal sensing, and heating features on single small-sized UCNPs (<10 nm) is still worth further studies by engineering the core/shell design.

In Yb/Er upconversion systems, the NIR excitation light is mainly absorbed by the sensitizer Yb3+. The absorbed energy can be released through three possible routes: energy transfer to Er3+ ions for upconversion emissions, downconversion luminescence, and nonradiative transition (Figure 1). Nonradiative transitions, between various energy levels of Er3+ ions or between excited and ground states of Yb3+ ions, are responsible for the heat generation in Yb/Er codoped nanoparticles. One straightforward way to enhance the heating capability is to increase their absorption coefficients and nonradiative transition rates through the incorporation of high-concentration Yb3+ ions into UCNPs. Unfortunately, the homogeneous doping of Yb3+ ions at high levels will result in
the decline of UCL due to the concentration quenching effect. Spatial separation distribution between sensitizer and emitter ions by the core/shell design provides an effective approach to maintain the UCL intensity and at the same time enhance the heating capability of UCNPs. Herein, NaGdF₄:Yb/Er@NaYbF₄ and NaGdF₄:Yb/Er@NaGdF₄:Nd/Yb core/shell UCNPs with smaller sizes (<10 nm) were successfully synthesized by a layer-by-layer strategy. The shell highly doped with Yb³⁺ or Nd³⁺ ions could play a variety of roles: transferring the harvested energy to the emission core, protecting the core from the surface quenching, and acting as a heating unit (Figure 1a). The Yb/Er codoped core provided UCL and temperature sensing features. The Yb³⁺ or Nd³⁺-sensitized core/shell UCNPs were demonstrated to simultaneously show promising UCL, temperature sensing and photothermal conversion properties under 980 or 808 nm excitation, respectively. Especially, NaGdF₄:Yb/Er@NaGdF₄:Nd/Yb core/shell UCNPs could be excited by the light at a more biocompatible wavelength of 808 nm, and in this case the self-heating effect of water was greatly minimized. The
heating and sensing capabilities of the Nd³⁺-sensitized core/shell UCNP's were also investigated in aqueous environment under 808 nm excitation.

## RESULTS AND DISCUSSION

**Yb³⁺-Sensitized Core/Shell UCNP's.** Our previous work showed that NaGdF₄:Yb/Er UCNP's simultaneously possessed UCL, thermal sensing, and heating capabilities. However, they still need the relatively high-power laser for reaching a considerable temperature rise. Therefore, further studies are necessary to increase the heating capability of NaGdF₄:Yb/Er UCNP's without affecting their UCL properties. In Yb/Er codoped UCNP's, the excitation energy is mainly absorbed by Yb³⁺ ions. Except for energy transfer to Er³⁺ ions for upconversion emissions, the other unused absorption energy is dissipated via downconversion luminescence (DCL) and nonradiative transition of Yb³⁺ ions (Figure 1b). To improve the heating capability of NaGdF₄:Yb/Er UCNP's, one possible approach is to restrain the DCL process of Yb³⁺ ions. For this end, other acceptor ions (Ce³⁺, Dy³⁺, Ho³⁺, Nd³⁺, Tb³⁺, and Tm³⁺) were deliberately doped as quenching centers and their influences on photoluminescence and heat generation properties of NaGdF₄:Yb/Er nanoparticles were studied (Figure S1). These doping ions are chosen because they have close energy levels to the 2F⁵/₂ excited state of Yb³⁺. It was found that the incorporation of these acceptor ions had weak effects on the heating capability of NaGdF₄:Yb/Er UCNP's (Figure S1), probably due to inefficient energy transfer from Yb³⁺ to these doped ions. As could be found, the doping of these lanthanide ions resulted in the significant decrease of UCL; however, it had a relatively weak effect on the DCL of NaGdF₄:Yb/Er UCNP's (Figure S1). The UCL decline can be attributed to the cross relaxation process between Er³⁺ and these doped ions.⁴⁵−⁴⁷

With increasing the Yb³⁺ concentration in UCNP's, both the absorption rates to the excitation light and the nonradiative transition rates of Yb³⁺ ions will be increased. Therefore, it can be expected that the heating capacity will be greatly increased for NaGdF₄:Yb/Er UCNP's at high Yb³⁺ levels. However, high Yb³⁺ concentrations also will result in the decrease of UCL due to the concentration quenching effect and the back energy transfer from Er³⁺ to Yb³⁺.²⁹ To simultaneously achieve enhanced UCL and photothermal conversion properties, NaGdF₄:0.2Yb/0.02Er@NaYbF₄ (hereafter Yb/Er@Yb) active-core/active-shell UCNP's were designed and prepared via a layer-by-layer method.³⁸ Their spectroscopic, heating, and thermal sensing properties were investigated in comparison with the core nanoparticles. To maximize the light absorption rates of UCNP's, the Yb³⁺ concentration in the shell was set to 100%. As shown in Figure 2, well-dispersed NaGdF₄:Yb/Er core nanoparticles had an average diameter of ~5.6 nm. The size of Yb/Er@Yb core/shell UCNP's increased to ~9.6 nm after the NaYbF₄ shell growth, indicative of an active-shell thickness of ~2 nm. Both core-only and core/shell UCNP's were confirmed to show a hexagonal crystal structure (Figure S2). The NaYbF₄ shell in our study was grown by a successive layer-by-layer technique, and during the shell growth, the precursor concentration was kept low enough to restrain secondary nucleation. The Yb/Er@Yb core/shell structure was also beneficial for the synthesis of small-sized UCNP's with higher Yb³⁺ contents, as NaYbF₄ alone tended to grow into big nanoparticles unsuitable for many applications (>150 nm, Figure S3).

Figure 3a represents UCL spectra of core-only and core/shell NaGdF₄-based UCNP's dispersed in the cyclohexane solution. Excited at 975 nm, the UCL spectra were basically composed of green and red emission bands peaked at ~525, 545, and 660 nm, which could be assigned to ⁴I₁₁/₂ → ⁴I₉/₂, ⁴S₅/₂ → ⁴I₉/₂, and ⁴S₉/₂ → ⁴I₅/₂ transitions of Er³⁺, respectively (Figure 1b). It should be noted that the UCL intensity of Yb/Er@Yb core/shell UCNP's was ~10 times higher than that of the core nanoparticles. This significant UCL enhancement is due to the passivation action of the NaYbF₄ shell, which can effectively inhibit the quenching effect caused by surface defects or surface-attached ligands. In addition, the NaYbF₄ layer can absorb more excitation energy and then transfer to the NaGdF₄:Yb/Er core, thus leading to the increase in the UCL intensity.⁵⁹

The NaYbF₄ shell also can greatly increase the photothermal conversion properties of UCNP's. Under the 975 nm laser irradiation with a power density of ~7.6 W/cm², an obvious temperature rise (ΔT) was detected for the cyclohexane solution of Yb/Er-doped core or core/shell UCNP's (Figure 3b). Both the pure cyclohexane and the cyclohexane solution of pure NaGdF₄ nanoparticle (without the Yb/Er doping) exhibited a weak temperature increase of 1–2 °C at the same irradiation condition. It indicated that the measured temperature rise for Yb/Er-doped UCNP's was not caused by the direct absorption of the thermocouple to the laser radiation. The temperature rise of the cyclohexane solution of Yb/Er@Yb core/shell UCNP's was up to ~11.5 °C, significantly higher than in the case of NaGdF₄:Yb/Er core UCNP's (~4.9 °C). The increase in the heating capability of core/shell UCNP's is attributed to their increased absorption to the 975 nm light, arising from the introduction of the NaYbF₄ shell. Moreover, because the Yb³⁺ concentration in the shell is extremely high, the nonradiative transition probability is increased and the shell can effectively act as a heating unit. The results confirm that the emission-core/heating-shell design provides a promising solution for the simultaneous enhancement of UCL and heating capabilities on NaGdF₄-based UCNP's.

Figure 3c shows temperature-dependent green emission spectra of the cyclohexane dispersion of Yb/Er@Yb UCNP's. With the rise of temperature, the relative contribution of the 525 nm emission band also increased. It is due to the fact that ⁴H₁₁/₂ and ⁴S₅/₂ energy levels of Er³⁺ ions are thermally coupled and the relative population of these two excited states follows a typical Boltzmann's distribution. The intensity ratio (R⁴S₅/₂) from 525 nm (⁴H₁₁/₂ → ⁴I₉/₂) and 545 nm (⁴S₅/₂ → ⁴I₅/₂) emission bands can be written as

\[ R_{4S5/2} = C \exp(-\Delta E/kT) \]

where ΔE is the energy separation between ⁴H₁₁/₂ and ⁴S₅/₂ levels, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( C \) is a constant. On the basis of temperature-dependent UCL spectra, the ln(R⁴S₅/₂) versus \( 1/T \) relationship of Yb/Er@Yb core/shell UCNP's was calculated and shown in Figure 3d. According to eq 1, a good linear relationship (ln R⁴S₅/₂ = 1.96 – 940.5/S(T)) could be fitted, indicating that Yb/Er@Yb core/shell nanoparticles were applicable for temperature measurements through monitoring the intensity ratios of two green emission bands.

Because of very high Yb³⁺ levels in the shell of Yb/Er@Yb core/shell UCNP's, the back energy transfer from Er³⁺ to Yb³⁺ probably occurs at the interface between the core and shell, thus affecting the UCL efficiency of core/shell CUNP's. We also...
synthesized NaGdF₄:0.2Yb/0.02Er@NaGdF₄@NaYbF₄ (named as Yb/Er@Gd@Yb) active-core/inert-shell/active-shell UCNPs (size ∼12.5 nm, Figure S4), in which the inert NaGdF₄ layer was introduced to suppress the back energy transfer from Er³⁺ ions in the core to Yb³⁺ ions in the NaYbF₄ shell. As shown in Figure 3a, the UCL of Yb/Er@Gd@Yb UCNPs was more intensive by a factor of approximately 3 than that of Yb/Er@Yb nanoparticles. However, the incorporation of the NaGdF₄ layer resulted in the decrease of the heating capability. As shown in Figure 3b, the temperature increase of the cyclohexane solution of Yb/Er@Gd@Yb UCNPs was up to ∼9.0 °C, lower than that of Yb/Er@Yb UCNPs at the same irradiation condition. The decline in the heating capability for Yb/Er@Gd@Yb UCNPs is due to the fact that the inert NaGdF₄ layer (thickness ∼2 nm) dilutes the system and thus reduces the effective heating volume of UCNPs.

As can be observed, both UCL and photothermal conversion properties of NaGdF₄-based UCNPs can be improved by the introduction of the NaYbF₄ shell. These Yb³⁺-sensitized core/shell UCNPs simultaneously possess thermal sensing, enhanced upconversion emission, and heating capacities, thus showing a good prospect for practical applications in various fields. However, the absorption band of the sensitizer Yb³⁺ is located at ∼980 nm, which is overlapped with the absorption band of water. Continuous irradiation near 980 nm also would lead to the significant temperature increase of water (∼18 °C, Figure S5). In this case, Yb³⁺-sensitized UCNPs with multiple functions are limited to be used in nonaqueous environment or in solid state, such as for anticounterfeiting applications.²⁵,²⁶ For applications in the biomedical field, the water absorption to the ∼980 nm laser will cause possible thermal damages to normal biological tissues.⁴⁰⁻⁴² UCNPs that can be excited at more biocompatible wavelengths within so-called biological windows⁴⁰ and at the same time possess promising UCL/sensing/heating properties will be highly desired for biomedical applications.

Nd³⁺-Sensitized Core/Shell UCNPs. Nd³⁺-sensitized UCNPs can be effectively excited at more biocompatible wavelengths near 800 nm, and in this case, the laser-induced heating effect of water will be obviously reduced in comparison to that under conventional ∼980 nm excitation.⁴⁰⁻⁴⁶ Meanwhile, the absorption cross section of Nd³⁺ ions at ∼800 nm is 10 times higher than that of Yb³⁺ at ∼980 nm,⁴¹ which also favors the UCL and photothermal conversion processes. Herein, UCL, photothermal conversion, and temperature sensing properties of Nd³⁺-sensitized core/shell UCNPs with smaller sizes (<10 nm) were also investigated.

NaGdF₄:0.2Yb/0.02Er@NaGdF₄:0.1Yb/xNd core/shell nanoparticles (hereafter Yb/Er@Yb/Nd, x = 0.1−0.7) were successfully synthesized through a layer-by-layer procedure (Figure 4a−c). For the target of increasing the energy transfer efficiency from Nd³⁺ ions in the shell to Yb³⁺ ions in the core, the Yb³⁺ ions with a concentration of 10 mol % were also doped into the shell. The sizes of Yb/Er@Yb/Nd core/shell nanoparticles increased to ∼9.6 nm in comparison with core nanoparticles (∼5.6 nm, Figure 2a), implying a NaGdF₄:Yb/Nd shell thickness of ∼2 nm. The X-ray diffraction (XRD) measurements showed that all the Yb/Er@Yb/Nd samples had a hexagonal crystal structure (Figure 4d). With increasing the Nd³⁺ concentration x, the XRD peaks of core/shell UCNPs...
shifted to lower values of the diffraction angle, indicative of the increase of crystal interplanar spacing due to the larger atomic radius of Nd3+ (0.1123 nm) than that of Gd3+ (0.1075 nm).

In Yb/Er@Yb/Nd core/shell UNCPs, the excitation energy is mainly absorbed by Nd3+ ions and then transferred to Er3+ ions in the core through the Nd3+ → Yb3+ → Er3+ path, leading to upconversion emissions of Er3+ ions (Figure 1b). Therefore, the Nd3+ content in the shell has a direct and significant effect on the UCL properties of Yb/Er@Yb/Nd UCNPs. As shown in Figure 5a,b, the UCL intensities of Yb/Er@Yb/xNd UCNPs ($x = 0.1\rightarrow0.7$) increased with increasing the Nd3+ concentration ($x$), reaching a maximum at $x = 50$ mol %. A further increase in the Nd3+ concentration resulted in the decline of the UCL intensity. An optimized intensity at the Nd3+ concentration of 50% results from the competition among various energy transfer processes.47 First, the UCL process will benefit from higher Nd3+ levels, at which both the absorption rate of UCNPs and the energy transfer rate from Nd3+ to Yb3+ are increased. However, at higher Nd3+ concentrations, the deactivation process of Nd3+ ions also will be accelerated due to the increased cross relaxation between them. A balanced effect might occur at an optimized Nd3+ concentration of 50%, beyond which the detrimental effect surpasses the beneficial effect and thus results in the UCL decline. In addition, the harvested energy of Nd3+ ions also can be deactivated by the surface quenching process. To obtain strong upconversion emissions, higher Nd3+ concentrations are needed for the smaller-sized core/shell nanoparticles because of the increased surface quenching effect to Nd3+ ions. Consequently, the optimized Nd3+ concentration ($\sim$50%) in this work is higher than the reported values ($\sim$30%) in the Nd3+-sensitized NaYF4-based core/shell UCNPs with larger particle sizes.47,48

Except for the UCL, part of absorption energy of Nd3+ ions can be released in heat through the nonradiative deactivation process. The Nd3+-doped shell of Yb/Er@Yb/Nd UCNPs also can behave as the heating unit, and the heating capacity of nanoparticles is demonstrated in Figure 5c,d. Figure 5c illustrates the temperature rise curves of Yb/Er@Yb/xNd nanoparticles dispersed in cyclohexane ($\lambda_{ex} = 808$ nm, power density: $\sim7.6$ W/cm²). It should be noted that the pure cyclohexane solution exhibited a negligible temperature rise ($\Delta T \sim 1$ °C) under 808 nm excitation. The obvious temperature rise ($\Delta T$) could be detected for the cyclohexane solution containing Nd3+-sensitized core/shell nanoparticles. For instance, the temperature rise of Yb/Er@Yb/0.5Nd nanoparticles dispersed in cyclohexane was up to $\sim10.2$ °C when exposed to the 808 nm laser over a period of 15 min. The heating capacities of Yb/Er@Yb/xNd core/shell UCNPs increased monotonously with increasing the Nd3+ concentration (Figure 5d). The laser-induced temperature rise ($\Delta T$) depends on the harvested excitation energy by UCNPs as well as the proportion of absorbed energy dissipating in heat. Both absorption coefficients and nonradiative transition rates are increased at higher Nd3+ concentrations, resulting in the enhancement of the heating capacity of core/shell UCNPs. The strong Nd3+ concentration dependence of heating capacity also reveals that the Nd3+-doped shell is the main responsible source for the temperature increase of the nanoparticle solution when irradiated with the 808 nm laser.

The cyclohexane dispersion of Yb/Er@Yb/0.7Nd UCNPs exhibited a temperature rise of $\sim12.7$ °C under 808 nm excitation with a power density of $\sim7.6$ W/cm², higher than that of Yb/Er@Yb UCNPs ($\sim11.5$ °C) under the same measuring conditions except excitation at 975 nm. It should be noted that Nd3+ ions are only distributed in the shell of Yb/
Er@Yb/0.7Nd UCNPs and by a simple calculation, the average concentration of Nd³⁺ ions in Yb/Er@Yb/0.7Nd UCNPs is 35% lower than that of Yb³⁺ ions in Yb/Er@Yb UCNPs. The results indicate that Nd³⁺-sensitized UCNPs have an increased heating capacity than that of Yb³⁺-sensitized ones, owing to the relatively larger absorption cross section of Nd³⁺.

Figure 6a represents green emission bands of Er/Yb@Yb/0.5Nd nanoparticles upon 808 nm excitation at various temperatures. It was also found that the relative intensity of the ∼525 nm band increased with the rise of temperature. On the basis of the data of ln(R_HS) versus 1/T (Figure 6b), a linear relationship (ln(R_HS) = 2.26−1085.4/T) could be fitted according to eq 1. The results indicate that small-sized Er/Yb@Yb/Nd UCNPs (<10 nm) are also capable of simultaneously integrating UCL, temperature reading, and heating functions on single nanoparticles. However, because of the presence of oleate ligands on the nanoparticle surface, the hydrophobic UCNPs cannot be well dispersed in aqueous media. Therefore, surface modifications to render these oleate-capped UCNPs dispersible in the aqueous phase are needed prior to the biological applications.

**Temperature Sensing and Heating Properties of UCNPs in Water.** The temperature sensing and heating performances of Er@Yb/Nd UCNPs were further explored in the aqueous medium to mimic the intracellular measuring conditions. Water-soluble surface modifications of Nd³⁺-sensitized core/shell UCNPs were accomplished via a ligand-free method previously reported in the literature.⁴⁹ The oleate ligands attached to the surface of as-prepared Er/Yb@Yb/Nd UCNPs were removed through a straightforward acid treatment. The removal of oleic acid ligands from the particle surface could be confirmed by the disappearance of absorption peaks at ∼2924 and ∼2853 cm⁻¹ in Fourier transform infrared (FTIR) spectra (Figure S6), which originate from symmetric and asymmetric stretching vibration of methylene (−CH₂−) in long alkyl chain, respectively.⁴⁹,⁵⁰ The TEM image showed that after the removal of oleic acid, the morphology and mean particle size of Er/Yb@Yb/Nd UCNPs remain essentially unchanged and no obvious agglomeration was found (Figure S6). Ligand-free Er/Yb@Yb/Nd UCNPs could be well dispersed in water to form transparent colloidal solution, which was stable without obvious sedimentation (the inset of Figure S6).

Figure 7a shows the heating curves of aqueous solutions of Er/Yb@Yb/xNd UCNPs under 808 nm excitation (power density: ∼7.6 W/cm²); (b) plots of ln(R_HS) vs 1/T for the aqueous solution of Yb/Er@Yb/0.5Nd core/shell UCNPs.
On the basis of upconversion emission spectra of Er/Yb@Yb/0.5Nd UCNPs at various temperatures in the aqueous medium (Figure S7), the $\ln(R_{\text{HS}})$ values as a function of $1/T$ were calculated and shown in Figure 7b. In line with eq 1, a linear fitting ($\ln R_{\text{HS}} = 2.01 - 987.8/T$) was obtained in the aqueous solution. For these luminescent nanothermometers, the thermal sensitivity ($S_R$) can be described by the relative variation of the emission intensity ratios with temperature:\textsuperscript{27}

$$S_R = \frac{1}{R_{\text{HS}}} \frac{dR_{\text{HS}}}{dT}$$

(2)

On the basis of the data shown in Figure 7b, the thermal sensitivity of Er/Yb@Yb/0.5Nd UCNPs in water was calculated to be about $1.2 \times 10^{-2}$ °C$^{-1}$ at 30 °C, which was close to the thermal sensitivities reported in other Er$^{3+}$-activated UCNPs.\textsuperscript{32,48} It should be noted that the thermal sensitivity of green emissions of Er$^{3+}$ ions does not vary significantly with changes in the sensitization ions (Yb$^{3+}$ or Nd$^{3+}$) or the dispersing media (water or cyclohexane) (Figure S8). The above results indicate that Er/Yb@Yb/Nd UCNPs with small sizes (<10 nm) are able to behave, at the same time, as luminescent probes, temperature nanosensors, and heating agents. Moreover, Er/Yb@Yb/Nd UCNPs are excitable at ~800 nm and will be more suitable for the biological applications by avoiding the self-heating effect of water. This combination makes Er/Yb@Yb/Nd UCNPs more promising single platforms for dynamically controlled thermal treatments under the single-wavelength laser excitation.

### CONCLUSIONS

NaGdF$_4$:Yb/Er@NaYbF$_4$ and NaGdF$_4$:Yb/Er@NaGdF$_4$:Yb/Nd core/shell UCNPs with smaller sizes (<10 nm) were successfully prepared via a layer-by-layer strategy. Upconversion emission, temperature sensing, and heat generation properties of these UCNPs were investigated. The NaYbF$_4$ shell could play the role of a heating unit and at the same time protected the emission core from the surface-related quenching effect. Therefore, enhanced heating capability, increased UCL intensities, and good temperature sensing properties were achieved on single core/shell UCNPs of NaGdF$_4$:Yb/Er@NaYbF$_4$. For NaGdF$_4$:Yb/Er@NaGdF$_4$:Yb/Nd core/shell UCNPs, the highly Nd$^{3+}$-ion doped shell behaved as the heating unit and simultaneously transferred absorption energy to the core for upconversion emissions. The strong dependencies of photothermal conversion and UCL properties on the Nd$^{3+}$ content in the shell were revealed. Nd$^{3+}$-sensitized core/shell UCNPs with 808 nm excitation showed much lower heating effect of water, and their heating and temperature reading capabilities were demonstrated in the aqueous medium. These core/shell UCNPs were able to simultaneously act as luminescent probes, heating agents, and temperature nanosensors, showing great potential for applications in imaging-guided and temperature-monitored photothermal treatments.

### EXPERIMENTAL SECTION

#### Synthesis of Core-Only and Core/Shell UCNPs.

NaGdF$_4$:Yb/Er core nanoparticles were synthesized using a co-precipitation method.\textsuperscript{31} Lanthanide acetates, sodium hydroxide, and ammonium fluoride were used as starting materials, which reacted at 295 °C in the mixed solvents of oleic acid (OA) and 1-octadecene (ODE) to prepare core nanoparticles. A modified layer-by-layer method was adopted to synthesize NaGdF$_4$:Yb/Er@NaYbF$_4$ and NaGdF$_4$:Yb/Er@NaGdF$_4$:Nd core/shell UCNPs.\textsuperscript{38} Sodium trifluoroacetate and lanthanide acetates were dissolved in OA and the OA/ODE mixture, respectively, to prepare the shell precursors. Subsequently, certain amounts of the shell precursors were alternately injected to the reaction solution containing the as-prepared core nanoparticles to synthesize core/shell UCNPs. The reaction temperature for the shell growth was decreased to 290 °C to avoid homogeneous nucleation. Detailed synthesis procedures and parameters could be found in our previous work.\textsuperscript{26,29}

#### Preparation of Ligand-Free UCNPs.

A previously reported ligand-free protocol was used to transfer oleate-capped NaGdF$_4$:Yb/Er@NaGdF$_4$:Nd/Yb UCNPs into the aqueous phase.\textsuperscript{45} First, oleate-capped core/shell nanoparticles (50 mg) were dispersed in 10 mL of deionized water and then the HCl aqueous solution (0.1 M) was added drop wise to adjust the pH value to 4. Subsequently, the mixed solution was sonicated for 2 h at the pH value of 4 to protonate the carboxylate groups of oleate ligands. In the following, the aqueous solution was blended with diethyl ether and the generated oleic acid molecules were removed by extraction. The procedure was repeated several times until the solution became totally clear. The ligand-free nanoparticles were separated by centrifugation at 9000 rpm after precipitation with acetone. After washing several times with acetone, the ligand-free core/shell UCNPs were finally dispersed in deionized water to form a transparent solution.

#### Characterization.

A Tecnai G2 transmission electron microscope was used to observe the particle size and morphology. The crystalline phase of UCNPs was determined by X-ray diffraction (XRD) measurements on a Shimadzu XD-3A X-ray diffractometer. Fourier transform infrared (FTIR) spectra of UCNPs were measured on a Nicolet 5700 FTIR spectrometer. Continuous 975 or 808 nm diode lasers were used as the light sources for UCL spectra and photothermal conversion measurements. The nanoparticle solution was added into a 10 mL quartz cuvette, and UCL spectra under the laser irradiation were measured by a Maya2000Pro portable spectrometer. For temperature-dependent UCL spectra measurements, the quartz cuvette containing the nanoparticle solution was heated by a resist-heating hot stage and the temperature was determined by a thermocouple that was immersed into the nanoparticle solution. For photothermal conversion measurements, the volume of the nanoparticle solution was fixed at 2 mL, with the concentration of 20 mg/mL. The diameter of the laser beam at the sample position was ~5 mm, and the laser power density was ~7.6 W/cm$^2$. The temperature rise of the nanoparticle solution during the laser irradiation was measured by a thermocouple with an accuracy of ±0.1 °C.

#### ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01581.

Upconversion/downconversion luminescence spectra and heating curves of NaGdF$_4$:Yb/Er nanoparticles doped with various ions; XRD patterns of Yb/Er@Yb nanoparticles; TEM image of NaYbF$_4$, NaGdF$_4$:Yb/Er@NaGdF$_4$:Nd and ligand-free Yb/Er@Nd nanoparticles; heating curves of water under 975 or 808 nm...
excitation; FTIR spectra of oleate-capped and oleate-free Nd3+-sensitized nanoparticles; temperature-dependent UCL spectra of ligand-free Yb/Er@Yb/Nd UCNP’s and thermal sensitivities of nanoparticles in different environments (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China (51302038), the Natural Science Foundation of Jiangsu Province of China (BK20160073), the Fundamental Research Funds for the Central Universities (2242016K400102), the Jiangsu Key Laboratory for Advanced Metallic Materials (BM2007204), and the Jiangsu Key R&D Program (BE2015102).

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