Dual-emitting nanocomposites derived from rare-earth compound nanotubes for ratiometric fluorescence sensing applications†

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A new class of ratiometric fluorescence sensors composed of rare-earth (RE) compound nanotubes is described. Polyethylenimine-coated yttrium hydroxide fluoride nanotubes (YHF NTs) that were synthesized hydrothermally exhibit highly efficient fluorescence when doped with RE ions. The polyethylenimine on the NTs facilitates the incorporation of phosphors such as quantum dots or organic dyes onto the NT surface to produce dual-emitting nanocomposites which are excellent ratiometric fluorescence sensors. The phosphor layer and underlying tubes in the nanocomposites act as the indicator and reference probes, respectively. This ratiometric fluorescence method which can be applied to the detection of heavy metals in solutions, temperature sensing, and pH sensing boasts high sensitivity and selectivity as well as better accuracy than traditional intensity-based fluorescence methods.

The integration of nanotechnology into sensing applications has had a great impact on the development of new nanomaterials and nanodevices.13 Hybrid nanocomposites have been regarded as promising ratiometric fluorescence sensors because they can integrate different kinds of fluorescent species into one common nanostructure, thus producing intriguing behavior and functionalities far beyond those of their individual counterparts.8,10,11 The fabrication of nanocomposites generally requires the pre-synthesis of specifically structured nano-architectures as first-stage nano-carriers, which should be optimized to load, protect, and distribute the second-stage small nanoparticles or molecules.14 The optical performance and loading ability of the first-stage nanostructures are both crucial to the fabrication of the nanocomposites with high performance in targeted fluorescence sensing applications.

As an important class of advanced nanomaterials, rare-earth (RE) compounds have received special research interests in recent years because of their attractive optical and chemical features.15–19 Unlike other commonly used phosphors such as semiconductor quantum dots (QDs) and organic dyes, the localized wave function of the RE ions in nanomaterials gives rise to unique size-independent fluorescence via f–f or f–d transitions.20 Together with other desirable properties such as a large Stoke’s shift, long fluorescence lifetime, and up-converted fluorescence, their monochromaticity and resistance to photobleaching properties are especially important to sensing and labeling applications.15,21–27 In recent years, various RE compounds such as fluorides, oxides, and hydroxides have been synthesized and their fluorescence imaging and sensing applications have been extensively investigated.16,18,28–30 However, there have been few reports on the preparation of nanocomposites

1 Introduction

Fluorescence methods are inherently sensitive, diverse, nondestructive, convenient and have many applications in real-time and in situ sensing. Intensity-based fluorescence sensing is currently the dominant analytical tool and is widely used in chemical analysis, environmental monitoring, and biological detection. However, in order to ensure high accuracy and effectiveness, certain issues about the measurement process must be addressed. Typically, intensity-based fluorescence sensors consisting of a single probe are prone to errors due to unpredictable factors such as fluctuated light source intensity, instrumental drift, variations in excited sensors, and probe photobleaching.2 On the other hand, ratiometric fluorescence measurements incorporating an insensitive reference probe can avoid some of these problems thereby offering more accurate detection.3–11 In ratiometric detection, the fluorescence intensity from an indicator probe is divided by the intensity measured by the reference probe. Hence, the results are less dependent on uncontrolled variables and it can be performed without using expensive lifetime measurement systems.12

Notes

† Electronic supplementary information (ESI) available: EA and TGA profiles, emission spectra of YHF:Eu NTs. See DOI: 10.1039/c2nr33217e
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using RE nanomaterials as carriers. This may stem from the difficulty to fabricate RE nanomaterials with good fluorescence performance and loading ability for the second-stage materials.

In this paper, we report a polyethylenimine (PEI) assisted hydrothermal route to synthesize RE-doped yttrium hydroxide fluoride NTs (YHF NTs) with a tubular morphology having free amino groups on the rough surface and highly efficient fluorescence. A new class of dual-emitting nanocomposites is produced by using the RE-doped YHF NTs as the carriers to load fluorescent QDs or organic dyes. The nanocomposites are utilized as ratiometric fluorescence probes in heavy-metal ion, temperature, and pH sensing according to the properties of the corresponding host and guest materials. Our results reveal that the technique has high sensitivity and selectivity as well as better accuracy than traditional intensity-based fluorescence sensing methods.

2 Experimental section

2.1 Materials

YCl3, CeCl3, TbCl3, EuCl3 and PEI (MW = 10 000) were purchased from Sigma-Aldrich. The other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. All the reagents were used as received without further purification and ultrapure water was used throughout the experiments.

2.2 Synthesis of the RE compound NTs

LnCl3 (Ln = Y, Ce, Tb, Eu) was dissolved in ultrapure water with a concentration of 0.5 M. In a typical procedure to synthesize cerium-doped yttrium hydroxide fluoride NTs [YHF:31% Ce NTs, Ce/(Ce + Y) molar ratio = 31%], 0.25 mL of YCl3, 0.1 mL of CeCl3, and 0.325 mL of NH4F (1 M) were dissolved in 7.0 mL of ethanol and 12.0 mL of water. A solution of 1.0 mL of PEI (10 wt%) was added to form a milky-white suspension under vigorous stirring for 5 min under nitrogen. The mixture was then sealed in a Teflon-lined autoclave (50 mL capacity) and heated to 180 °C for 7 h. 456.8 mg of CdCl2·2.5H2O and 382.1 mg of MPA were dissolved in 100 mL of ultrapure water and the pH was adjusted to 10.0 by adding 2 M NaOH. Afterwards, the oxygen-free solution containing NaHTe was added to the precursor solution above and stirred vigorously. The mixture was then transferred to a Teflon-lined autoclave (50 mL capacity) and heated at 180 °C for 7 h. After heating for 50, 65 and 80 minutes, green, yellow, and red CdTe QDs were formed, respectively. After heating was stopped, the samples were cooled to room temperature by a hydro-cooling process. The synthesized QDs were directly used in the next procedure without washing.

2.3 Synthesis of the CdTe QDs

The CdTe QDs were synthesized in water using 3-mercaptopropionic acid (MPA) as a stabilizer. Briefly, 80 mg of sodium borohydride (NaBH4) was dissolved in 2 mL of ultrapure water and reacted with tellurium to prepare sodium hydrogen telluride (NaHTe). 127 mg of tellurium powder was added quickly. After, the reaction proceeded in an ice-water bath for 0.5 h under flowing nitrogen, then the bottle was sealed and refrigerated at 4 °C for 7 h. 456.8 mg of CdCl2·2.5H2O and 382.1 mg of MPA were dissolved in 100 mL of ultrapure water and the pH was adjusted to 10.0 by adding 2 M NaOH. Afterwards, the oxygen-free solution containing NaHTe was added to the precursor solution above and stirred vigorously. The mixture was then transferred to a Teflon-lined autoclave (50 mL capacity) and heated at 180 °C for 7 h. After heating for 50, 65 and 80 minutes, green, yellow, and red CdTe QDs were formed, respectively. After heating was stopped, the samples were cooled to room temperature by a hydro-cooling process. The synthesized QDs were directly used in the next procedure without washing.

2.4 Loading of QDs onto the RE NTs

The CdTe–YHF NTs were synthesized by ultrasonic treatment. 0.5 mL of CdTe QDs were mixed with 1 mL of YHF NTs. The mixture was stirred mechanically and then sonicated in a bath for 30 min. A KQ-100E ultrasonic cleaner (Jiangsu Kunshan Ultrasonic Instrument Co., Ltd) operated at 40 kHz with an input power of 100 W was employed. The experiments were carried out under ambient water temperature (30 °C) in an ultrasonic bath. The water in the ultrasonic bath was changed periodically to avoid temperature increase. The ultrasonic cycle consisted of 10 min of power-on followed by 20 s of power-off. The cycle was repeated three times. The nanocomposites were obtained by centrifugation at 10 000 rpm for 5 min before being re-dispersed in 1.0 mL of water.

2.5 Loading of FITC onto the RE NTs

The targeted organic dyes were dissolved in an appropriate amount of ultrapure water. Typically, a mixture containing 1.0 mL of 1.0 g L⁻¹ FITC (fluorescein isothiocyanate) and 1.0 mL of aqueous YHF NTs was stirred mechanically and then sonicated for 20 min. Ultrasonic treatment was carried out using the same procedure, except that the ultrasonic cycle was conducted twice. The nanocomposites were obtained by centrifugation at 10 000 rpm for 5 min before being re-dispersed in 1.0 mL of water.

2.6 Heavy-metal ion sensing

50 µL of CdTe–YHF:Ce NTs were added to 3 mL of solutions with different Cu²⁺ concentrations of 0, 0.5, 0.75, 1.0 and 1.25 nM. The resulting mixtures were incubated for 30 min while being stirred at room temperature, and then the fluorescence signals were collected. The sensing selectivity was determined by using 3 mL of 5 nM Cu²⁺, Ag⁺, Pb²⁺, Sr²⁺, Mn²⁺, Fe³⁺, Ca²⁺, Na⁺ and Li⁺ ions as the samples with the same procedure.

2.7 Temperature sensing

The temperature-dependent fluorescence spectra were recorded using a fluorescence spectrophotometer equipped with a
thermostated cuvette holder to hold 2 mL of CdTe–YHF:Ce NT solution. The real temperatures of the samples were measured by a thermometer immersed in the solution. The spectra were recorded 2 min after the solution temperature reached 303, 313, 318, 323, 328, 333, 338, 343, 348 and 358 K, respectively.

2.8 pH sensing

The pH of a 2 mL aliquot of FITC–YHF:Ce,Tb NTs solution was regulated by adding 1 M HCl or 1 M NaOH, and measured by a pH meter. The fluorescence spectra were recorded after the pH reached 5.4, 5.8, 6.2, 6.9, and 7.5.

2.9 Characterization

The H, C and N concentrations in the samples were determined by a Vario EL III Element Analyzer. The total Y content was measured by inductively coupled plasma (ICP) optical emission spectroscope on a Thermo Electron IRIS Intrepid II XSP. The Ce and F contents in the samples were determined by a field-emission scanning electron microscope (FESEM, Siron, FEI) equipped with an energy dispersive X-ray spectrometer (SEM/EDS). Multi-techniques were used to determine the formula of the samples according to the generally used method for such RE compounds. The thermogravimetric analysis (TGA) traces were recorded on a PerkinElmer Diamond-DSC thermal analyzer and powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8-advance X-ray diffractometer with Cu Kα1 irradiation (λ = 1.5406 Å). The Fourier transform infrared (FTIR) spectra were acquired on a NICOLET 5700 FTIR spectrometer. The morphology and structure of the products were observed on a field-emission scanning electron microscope (FE-SEM, Siron, FEI), a JEM 2010 HT transmission electron microscope (TEM), and a JEM 2100F field emission transmission electron microscope (HR-TEM). The absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrophotometer. The excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp as the excitation source. The true-color fluorescence images were obtained by a fluorescence microscope (Olympus IX71) equipped with a 40× objective lens. A color charged-coupled device camera was used to capture the microscopic photoluminescence images.

3 Results and discussion

3.1 Physical properties of the RE compound NTs

3.1.1 Composition and structure. The RE compound NTs were synthesized hydrothermally. Typically, the composition of the YHF:31% Ce NTs was determined by TGA and elemental analysis (EA) (see Fig. S1 in the ESI†). The chemical constituents of the NTs are: calculated (%): Y 38.76, Ce 27.39, F 15.80, H 1.06, H2O 0; found (%): Y 36.15, Ce 28.37, F 15.80, H 0.889, H2O 0. Based on these data, the empirical formula of the YHF:31% Ce NTs is [Y0.69Ce0.31](OH)1.682F1.318.

The crystal structure determined by XRD is depicted in Fig. 1a in which the peak positions agree well with those of hexagonal-phase Y(OH)1.69F1.31 (JCPDS standard card 80-2006). The intense and narrow reflections from (100), (110), and (101) together with a number of minor reflections from all other planes of the hexagonal structure indicate high crystallinity and that the synthesized YHF:31% Ce has a crystal structure similar to that of Y(OH)1.69F1.31. It should be noted that the high concentration of Ce3+ does not affect the structure of the YHF NTs. As shown in Fig. 1c and d, the YHF:Ce NTs have tubular structures with outer diameters of about 300 nm, lengths of about 6.0 μm, and wall thicknesses of about 50 nm. The hexagonal prism morphology is similar to that reported previously for hexagonal-phase Y(OH)1.69F1.31 NTs. The crystal structure of the YHF:Ce NTs was further investigated by HR-TEM. The lattice fringe in Fig. 1b shows that the two sets of distinct interplanar distances of 0.3035 nm and 0.2949 nm are in good agreement with the d spacing of the (110) and (101) lattice planes of hexagonal Y(OH)1.69F1.31. It was further confirmed by the corresponding FFT pattern acquired from the indicated square area (inset in Fig. 1b). There is a highly symmetrical dotted lattice, which can be indexed to a hexagonal Y(OH)1.69F1.31 single crystal, revealing the single-crystalline nature of the synthesized YHF:Ce NTs.

3.1.2 Surface properties. The surface chemistry of the YHF:Ce NTs is investigated by FTIR. The PEI which has multiple amino groups on each polymer chain plays a vital role in the formation of NTs with favorable surface properties. As shown in Fig. 2, the effect of PEI on the NTs surface is demonstrated by the presence of absorption bands from the internal vibration of the NH2 bonds (1386–1430 cm−1) and CH2 stretching vibrations (2854–2962 cm−1). The intense absorption peak at about 1452 cm−1 corresponds to amine groups, suggesting that there are free amino groups on the particle surface. The characteristic O–H vibrations are also observed at around 3634 and 3444 cm−1, which can be ascribed to the stretching vibration of

![Fig. 1](image-url)
a virtually free hydroxyl species and mostly hydroxyl species which form hydrogen bonds with their fluorine or oxygen neighbors, respectively. A band at around 770 cm$^{-1}$ is assigned to the O–H deformation bands. Furthermore, the YHF:Ce NTs have a hollow tubular structure and rough surface [inset image (left) in Fig. 2] which provides a larger surface area than traditional nanostructures, such as nanoparticles, nanorods, etc.$^{16,32}$ The enhanced surface properties enable the incorporation of second-stage materials by conjugation protocols. The right inset image in Fig. 2 shows the homogeneous dispersion of the NTs in water, forming a stable solution.

### 3.1.3 Absorption and fluorescence properties

Bright fluorescence from the YHF NTs is achieved by doping with RE ions such as Ce$^{3+}$, Eu$^{3+}$, and Ce$^{3+}$/Tb$^{3+}$. As shown in Fig. 3a, the absorption spectrum of the YHF:Ce NTs contains four absorption peaks at 252, 234, 217, and 206 nm, which are attributed to the Ce$^{3+}$ f-d electron transitions.$^{44}$
Correspondingly, a broad and strong peak at 255 nm is found from the excitation spectra. Furthermore, under 255 nm excitation, the emission spectra of YHF:14.3% Ce NTs show the characteristic emission from Ce$^{3+}$ at ~272 nm arising from the 5d–4f transition. Fig. 3b further shows the emission spectra of the YHF:14.3% Ce, x% Tb NTs ($x$ = 2.9, 5.7, 8.6, and 11.4). Under 255 nm excitation, the characteristic emission of Tb$^{3+}$ for the $^5D_{4} - ^7F_{J}$ transitions range from 475 nm to 650 nm together with the UV Ce$^{3+}$ emission. In general, the direct excitation of Tb$^{3+}$ ions is difficult and inefficient due to the Laporte forbidden f–f transition. Here, Ce$^{3+}$ also acts as the sensitizer which transfers energy to the co-doped Tb$^{3+}$ ions, resulting in the efficient Tb$^{3+}$ green emission. Therefore, when the Tb$^{3+}$ concentration is increased from 2.9% to 11.4%, the Ce–Tb energy transfer increases the Tb$^{3+}$ emission but reduces the Ce$^{3+}$ emission. The fluorescence properties of the YHF:Eu NTs are shown in Fig. S2 in the ESI.

The quantum yield of these RE-doped YHF NTs is determined by comparing the fluorescence from the YHF:14.3% Ce, 11.4% Tb solution to that from a solution of quinine bisulfate in 0.5 M H$_2$SO$_4$. By measuring the fluorescence from both the Tb$^{3+}$ and Ce$^{3+}$ ions, the quantum yield of the YHF:Ce,Tb NTs in the aqueous solution is found to be about 12.2%, which is as high as that reported for Ce,Tb co-doped RE fluoride NPs. The bright fluorescence from the YHF:Ce,Tb NTs is further illustrated by the fluorescence photo of the solution and micrograph of the NTs under UV light excitation (inset in Fig. 3b).

### 3.2 Fabrication of the dual-emitting nanocomposites

#### 3.2.1 QD–RE nanocomposites

Fig. 4a shows the schematic of the process to load the CdTe QDs onto the YHF:Ce NTs. The nanocomposites are labeled CdTe–YHF:Ce NTs. The negatively charged CdTe QDs are subsequently anchored onto the surface of the NTs via the electrostatic interaction with the positively charged PEI layer. The TEM results in Fig. 4b corroborate the success in attaching the QDs to the YHF:Ce NTs. The well-dispersed QDs decorate both the inner and outer walls of the NTs and the HR-TEM images in Fig. 4c clearly show the crystalline CdTe features on the surface of the YHF NTs. The corresponding FFT pattern acquired from the area indicated by a square is associated with CdTe. These data provide experimental evidence of the incorporation of QDs into the YHF:Ce NTs. The interaction between the QDs and NTs is quite strong because the nanocomposites are not removed during rinsing.

Fig. 5 displays the fluorescence characteristics of the QD–RE nanocomposites fabricated with YHF:Ce NTs and CdTe QDs of different sizes. Under 255 nm UV light excitation, the nanocomposites exhibit two types of emission: UV emission from the RE-doped NTs and visible size-dependent emission from the decorated CdTe QDs. Since the RE emission is in the UV region, the color of the fluorescence is determined by the decorated QDs. The fluorescence uniformity further confirms the successful loading of the QDs onto the RE compound NTs.

#### 3.2.2 FITC–RE nanocomposites

The RE compound NTs can also be used to load organic dyes using a similar method.
Fig. 6a shows the procedures to prepare FITC loaded YHF:Ce,Tb NTs which are designated as FITC–YHF:Ce,Tb NTs. Since the surface of the NT is coated with PEI, the isothiocyanate group of the FITC molecule can easily react with the primary amine of the PEI to form a thiourea bond which facilitates the loading of the FITC molecules. The fluorescence properties of the FITC–YHF:Ce,Tb nanocomposites are shown in Fig. 6b. Under 255 nm light excitation, the nanocomposites exhibit emission from the RE-doped NTs and green emission from the attached FITC molecules. The inset image in Fig. 6b further illustrates the uniformity of the fluorescence.

Our results demonstrate the successful loading of inorganic nanoparticles and organic molecules onto the RE NTs due to the enhanced surface properties of the NTs. First of all, the PEI on the surface enables the NTs to attach to inorganic/organic materials via electrostatic interaction and covalent bonding. Secondly, the NTs with a hollow tubular structure and rough surface can serve as an effective reservoir for the second-stage materials. Moreover, owing to the high loading ability on the RE NTs, fluorescence from the nanocomposites can be regulated by altering the phosphor layers and the RE ions in the host NTs, thus facilitating the design of different fluorescence sensors to cater for different applications.

3.3 Sensing applications

3.3.1 Heavy metal ion sensing. Because of the known fluorescence response of CdTe QDs to heavy metal ions such as Ag+ and Cu2+, the CdTe–YHF:Ce NTs were employed as probes to detect metal cations. Fig. 7a displays the emission spectra of the solution containing the CdTe–YHF:Ce NTs with different amounts of Cu2+. The CdTe emission at ~586 nm decreases gradually with an increase in the concentration of Cu2+, this is due to the replacement of Cd2+ on the surface of the QDs by Cu2+, which leads to the formation of a CuS precipitate on the surface or isolated Cu+ on the CdTe QDs. In contrast, the RE emission at 327 nm from Ce3+ remains constant as a result of the high chemical stability of the RE ions. Thus, the variation of the emission intensity ratio, \( I_{QD}/I_{RE} \), quantitatively indicates the concentration of Cu2+. As shown in the inset in Fig. 7a, a linear correlation is found between the Cu2+ concentration from 0 to 1.25 nM and \( I_{QD}/I_{RE} \) and a detection limit as low as ~0.5 nM can be inferred. The results indicate that the CdTe–YHF:Ce NTs constitute a high-sensitive ratiometric fluorescence sensor and the emission intensity ratio \( I_{QD}/I_{RE} \) quantitatively reveals the Cu2+ concentration in an aqueous solution. To demonstrate the selectivity of this ratiometric fluorescence sensor, several
different metal ions including Cu^{2+}, Ag^+, Pb^{2+}, Sr^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Na^+ and Li^+ at the same concentration of 5 nM were used to check their influence on the fluorescence characteristics (see Fig. 7b). It is found that only Ag^+ and Cu^{2+} decrease the IQD/IRE ratio, indicating the high selectivity of the ratiometric fluorescence sensor to heavy metal ions (Cu^{2+} and Ag^+). The accuracy of the ratiometric fluorescence sensing is assessed by comparing the results to those obtained by intensity-based fluorescence sensing. Fig. 7c and d show the relative standard deviation (RSD) of IQD and IQD/IRE obtained from repeated emission measurements of the same sample containing 50 nM Cu^{2+}. It is well known that fluorescence intensity measurements are susceptible to errors arising from instrumental drift. Here, a 7.5% RSD in the IQD measurement is calculated from the fluorescence intensity, but in contrast, only an RSD of 2.5% is obtained from IQD/IRE. The results demonstrate that the ratiometric fluorescence measurement utilizing the dual-emitting QD–RE nanocomposites has a higher precision and is less prone to instrumental drift compared to traditional intensity-based fluorescence sensing.

3.3.2 Temperature sensing. The temperature sensing capability of the CdTe–YHF:Ce,Tb NTs was also evaluated. As shown in Fig. 8a, as the solution temperature goes up, the CdTe emission diminishes gradually as a result of the thermal activation of the surface traps and subsequent non-radiative recombination. In contrast, the RE emissions remain nearly constant due to the high thermal stability. In our analysis, the intensity of the Tb^{3+} peak at 490 nm is adopted to represent the RE fluorescence intensity in order to generate the temperature-dependent emission intensity plot. Fig. 8d discloses a linear relationship between the temperature and IQD/IRE, demonstrating that IQD/IRE can be used to quantitatively determine the solution temperature. Fig. 8b and c further depict the change in the fluorescence color at 288 K and 338 K, respectively, suggesting that the fluorescence color can serve as a visual temperature indicator.

In traditional intensity-based fluorescence sensing measurements, the probe concentration must be kept constant because it affects the fluorescence intensity. On the other hand, in a ratiometric fluorescence sensing measurement, the emission intensity ratio IQD/IRE is unchanged as the concentration in the solution is increased, as shown in Fig. 8e. That is to say, although the quantity of the sensor added is varied and the initial amount of the targeted analytes is random, the intensity ratio of the two emissions is constant. This is another merit of ratiometric fluorescence sensing in contrast to intensity-based sensing.

3.3.3 pH sensing. We further demonstrate a sensitive and accurate ratiometric pH sensor by using the FITC–YHF:Ce,Tb NTs. As shown in Fig. 9a, the FITC–YHF:Ce,Tb NTs show RE emissions from Ce^{3+} and Tb^{3+} as well as FITC emission. As the

![Fig. 8](image8.png)  
Temperature sensing. (a) Emission spectra (λex = 255 nm) of CdTe–YHF:Ce,Tb NTs at different temperatures. (b and c) Photographs of the CdTe–YHF:Ce,Tb NTs at 288 K (b) and 338 K (c) under UV light irradiation. (d) Plot of temperature versus the fluorescence intensity ratio IQD/IRE of the nanocomposite probes. (e) Plot of probe amount versus the fluorescence intensity ratio IQD/IRE of the nanocomposite probes.

![Fig. 9](image9.png)  
pH sensing. (a) Emission spectra (λex = 255 nm) of the FITC–YHF:Ce,Tb NTs in the pH range from 5.4 to 7.5. (b) Plot of pH versus fluorescence intensity IQD/IRE of the FITC–YHF:Ce,Tb NTs.
pH decreases from 7.5 to 5.4, the emission intensity of FITC diminishes due to the interruption of fluorophore conjugation as a result of protonation, while the RE emission remains almost constant. For further quantitative analysis, the intensity at 521 nm was used to represent the FITC fluorescence intensity, and the Tb\(^{3+}\) peak at 543 nm was employed to represent the whole RE fluorescence intensity in order to generate the pH-dependent \(I_{\text{FITC}}/I_{\text{RE}}\) ratio plot (see Fig. 9b). The plot of pH versus \(I_{\text{FITC}}/I_{\text{RE}}\) exhibits an almost linear relationship in the pH range of 5.4–7.5. So the solution pH can be read out precisely by taking the \(I_{\text{FITC}}/I_{\text{RE}}\). Beyond that range, no linear relationship can be found from the sensor according to the properties of FITC. It should be noted that, the quantity of the probes or the targeted analytes can also be random in such pH sensing. These results indicate that the obtained FITC–YHF:Ce,Tb NTs can be applied in chemical and biological sensing as an ideal optical pH sensor. Furthermore, these results also suggest that different ratiometric fluorescence sensors can be fabricated by loading different fluorescent materials onto the NTs.

4 Conclusion

PEI-coated and RE-doped YHF NTs show highly efficient fluorescence characteristics. The RE compound NTs were used to incorporate QDs or organic dyes to produce a new class of dual-emitting nanocomposites. The phosphor layer and tubes in the nanocomposites serve as the indicator and reference probes, respectively, in ratiometric fluorescence sensing measurements pertaining to metal ions, pH, and temperature sensing. This ratiometric fluorescence technique based on the dual-emitting nanocomposites is highly efficient in various solution-based sensing applications. The advantages include: (i) high sensitivity and high selectivity, (ii) better accuracy than traditional intensity-based fluorescence sensing due to less instrumental drift, and (iii) flexibility in changing the probe concentration in quantitative sensing. The synthesis and technique can be readily extended to other types of dual-emitting nanocomposites for ratiometric fluorescence sensing applications.

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Notes and references