Talanta 120 (2014) 100–105

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Upconversion luminescence nanosensor for TNT selective and label-free quantification in the mixture of nitroaromatic explosives

Yingxin Ma, Leyu Wang*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Environmentally Harmful Chemical Analysis, School of Science, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 23 August 2013
Received in revised form
29 November 2013
Accepted 4 December 2013
Available online 10 December 2013

Keywords:
Upconversion luminescent nanoparticles
Label-free
TNT
Selective detection

ABSTRACT

This paper reports a rapid, sensitive, and selective nanosensor for the detection of 2,4,6-trinitrotoluene (TNT) in the mixture aqueous solution of nitroaromatics independent of immunoassay or molecularly imprinted technology and complicated instruments. Despite many strategies including immunoassay and molecularly imprinted technologies been successfully developed for the detection of TNT, it is not easy to differentiate TNT from 2,4,6-trinitrophenol (TNP) due to their very similar chemical structures and properties. In this work, the amine functionalized $NaYF_4$:Yb^{3+}/Er^{3+} upconversion luminescence nanoparticles (UCNPs) whose excitation (980 nm) and emission (543 nm) wavelength were far from the absorbance bands of other usual interference nitroaromatics including 2,4-dinitrotoluene (DNT), nitrobenzene (NB), and especially TNP, were utilized as the luminescent nanosensors for TNT luminescence detection. To make these UCNPs highly water stable and render the charge transfer from UCNPs to TNT easier, amino groups were introduced onto the surface of the UCNPs by coating a polymer layer of ethylene glycol dimethacrylate (EGDMA) hybridized with 3-aminopropyltriethoxysilane (APTS). After binding with TNT through amino groups on the UCNPs, the naked eye visible green upconversion luminescence of the UCNPs was dramatically quenched and thus a sensitive UC luminescence nanosensor was developed for TNT detection. However, other nitroaromatics including TNP, DNT, and NB have no influence on the green UC luminescence and thus no influence on the TNT detection. The luminescence intensity is negatively proportional to the concentration of TNT in the range of $0.01-9.0$ μg/mL with the 3σ limit of detection (LOD) of 9.7 ng/mL. The present studies provide a novel and facile strategy to fabricate the upconversion luminescence sensors with highly selective recognition ability in aqueous media and are desirable for label free analysis of TNT in mixed solution independent of immunoassay and molecularly imprinted technology and complicated instruments.

1. Introduction

Nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) have been widely used in many fields. Rapid, sensitive, and selective detection of trace 2,4,6-trinitrotoluene (TNT) has already attracted wide attention and is crucial for homeland security and public safety [1–13]. Up to now, various methods including LC–MS, GC–MS, HPLC, solid-phase microextraction (SPME), surface enhanced Raman spectroscopy (SERS), and desorption electrospray ionization (DESI) method have already been proposed for TNT assay [3,14–19]. Based on the color change of gold colloidal solution induced by TNT, Mao et al. developed a facile but sensitive method for the colorimetric visualization of TNT [20]. Moreover, fluorescent nanomaterials especially quantum dots (QDs) have drawn great attention and been widely developed to improve the sensitivity and selectivity to nitroaromatic detection due to their novel properties [12,21–25]. Zhang et al. have successfully developed these fluorescence quenching-based chemosensors which are suitable for the detection of nitroaromatic [6,8,9]. Based on the fluorescence resonance energy transfer (FRET), Goldman et al. demonstrated the fluorescence QDs nanosensor for the specific detection of TNT in aqueous environments [12]. Although the current methods for TNT detection have made significant advances [5,7,26–28], as the analog of TNT, the 2,4,6-trinitrophenol (TNP) often influence the detection of TNT. In order to increase the selectivity, immunoassay or molecularly imprinted technology were applied to the analysis of TNT. The TNP interference, however, was still not easy to overcome because of its highly similar chemical structure and properties in comparison with TNT [2,4–6,12,26,29]. Therefore, highly sensitive and selective detection of TNT from the mixture of nitroaromatics especially avoiding the influence of 2,4,6-trinitrophenol (TNP) is still a challenging work.

As complements to fluorescence dyes and QDs, rare earth doped upconversion (UC) luminescence nanomaterials have also been widely used in biomedical fields for UC luminescent

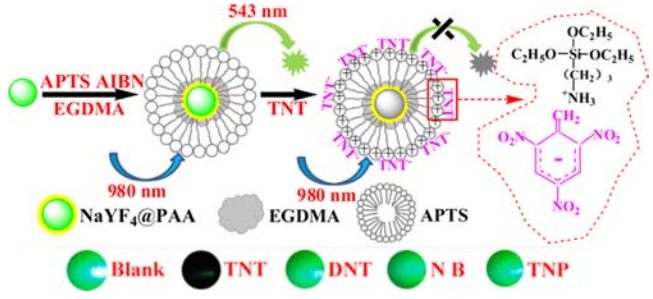
* Corresponding author. Tel./fax: 86 10 6442 7869.
E-mail address: lywang@mail.buct.edu.cn (L. Wang).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.12.009

quantification [30–33], in vitro and in vivo imaging [34–37] because of their special advantages including a large anti-Stokes shift of several hundred nanometers with 980-nm near infrared (NIR) excitation and visible-to-NIR emission, no autofluorescence from biological samples, remarkable NIR light penetration depth in tissue, and no photobleaching and thus, high photostability [38–55]. To the best of our knowledge, however, UC luminescent nanomaterials-based TNT selective luminescence sensor has seldom been reported [30]. Meanwhile, the nitroaromatics often absorb the light in the range of 200−400 nm, so, the selective detection of TNT in the mixture of nitroaromatics is difficult via colorimetric or fluorescent technology using UV–vis light as excitation [4,6,12]. Therefore, based on the selective quenching of UC emission instead of the excitation, the UC nanomaterials may be highly efficient luminescence nanosensors for TNT detection because the nitroaromatics cannot absorb the 980-nm light used for the irradiation of upconverting nanoparticles (UCNPs).

Based on this consideration, we developed a convenient and reliable UC luminescence means for the selective detection of TNT in the mixture solution of nitroaromatics containing TNT, TNP, 2,4-dinitrotoluene (DNT), and nitrobenzene (NB) with water-stable $NaYF_4$:Yb^{3+}/Er^{3+} UCNPs as luminescent nanosensors. As reported by Zhang, via a strong charge-transfer complexing interaction between amino groups on the QDs surface and electron-deficient TNT, the anionic form of TNT can absorb strongly the visible light leading to the fluorescence quenching of QDs [6,8]. As mentioned above, however, nitroaromatics absorb not only the emission but also the excitation in the range of UV–vis light, and thus interfere with the selective detection. To overcome this disadvantage, the amine functionalized $NaYF_4$:Yb^{3+}/Er^{3+} UCNPs with green emission centered at 543 nm via 980 nm irradiation were applied to the selective detection of TNT. Based on the energy transfer from the amine functionalized UCNPs to TNT, the green UC luminescence was dramatically and selectively quenched by TNT. Meanwhile, other nitroaromatics including TNP, DNT, and NB cannot absorb the 543 nm emission and 980 nm irradiation and thus no upconversion luminescence quenching can be observed. Based on the dramatic and selective quenching of the green UC luminescence of the UCNPs by TNT, a facile and selective UC nanosensor was successfully developed for TNT detection.

As shown in Scheme 1, to obtain efficient charge transfer from the amine of APTS on the UCNPs to TNT, form a visible light absorbent, and thus quench the UC green luminescence, the PAA coated $NaYF_4$:Yb^{3+}/Er^{3+} green upconversion luminescence nanocrystals were further functionalized with APTS to introduce the amino groups onto the UCNPs. It should be mentioned that no obvious quenching of the green UC luminescence by TNT can be observed before binding with amino groups; however, after binding with amine under basic conditions, the TNT solution becomes brown and absorbs the green upconversion luminescence markedly. Due to the PAA coating, these as-prepared UCNPs are highly water stable and can be coated with a thin layer of APTS by hydrolyzing the APTS in water. However, the coating shell of APTS is very thin and thus the amino groups are not enough for TNT binding, which limits the efficient luminescence quenching. So, the polymerization of EGDMA initiated by AIBN was conducted on the UCNPs surface. During this process, the APTS was hydrolyzed simultaneously and doped in the EGDMA polymer shell. Then more amino groups were successfully introduced on to the surface of upconversion $NaYF_4$ nanocrystals via this method. Under the irradiation of 980-nm light, the green upconversion luminescence (543 nm) of these amine functionalized UCNPs was selectively and dramatically quenched by TNT via the energy transfer from UCNPs to TNT. Meanwhile, the green UC luminescence was not influenced by the addition of other nitroaromatics including DNT, NB, and TNP (see the digital photos shown in Scheme 1). It is notable that the TNP has no influence on the green UC luminescence although it has very similar chemical structure and properties of TNT. Therefore, a very simple and highly selective UC luminescence nanosensor was developed for TNT detection independent of immunoassay and molecularly imprinted technology and complicated instruments.



Scheme 1. Scheme for the fabrication of upconversion $NaYF_4$:Yb^{3+}/Er^{3+} nanocrystals coated with amino groups and the UC luminescence quenching via adding TNT into the colloidal solution. Bottom row is the digital photographs obtained from the UCNPs colloidal solution in the presence of different nitroaromatics (9.0 μg/mL) under the irradiation of 980 nm diode laser. Only TNT quenched obviously the green UC luminescence of the NPs, suggesting a high selectivity for TNT detection.

2. Experimental section

2.1. Reagents and materials

2,4,6-Trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) were supplied by the National Security Department of China and recrystallized with ethanol before use. All other reagents are of analytical grade and used as received without further purification. 2,4-Dinitrotoluene (DNT) and nitrobenzene (NB) were purchased from Aladdin Chemistry Co. Ltd. $Y(NO_3)_3 \cdot 6H_2O$, $Er(NO_3)_3 \cdot 6H_2O$, and $Yb(NO_3)_3 \cdot 6H_2O$ (purity > 99.9%) were purchased from Beijing Ouhe Chemical Reagent Company. Poly(acrylic acid) (PAA, Mw=1800), 3-aminopropyltriethoxysilane (APTS), and ethylene glycol dimethacrylate (EGDMA) were obtained from Sigma-Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Tianjin Chemical Factory and used as azoinitiator. Ethanol, $NaHCO_3$, Na_2CO_3, NaOH, acetonitrile, ethylene glycol, NaF, NaAc, HAc, Na_2HPO_4, and NaH_2PO_4 were received from the Beijing Chemical Factory.

2.2. Characterization

The shape and size of the upconversion $NaYF_4$ nanocrystals before and after the amine functionalization were examined with an H-800 transmission electron microscope (TEM) with a tungsten filament at an accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-A112 X-ray diffractometer which employed Cu Kα radiation of wavelength λ=1.5418 Å. The operating current and voltage were kept at 40 mA and 40 kV, respectively. A 2θ range from 10° to 80° was covered in steps of 0.02° with a count time of 2 s. The photoluminescence measurements were carried out on an F–4600 spectrophotometer (Hitachi, Japan) equipped with a 980-nm diode laser with a fiber optic accessory (Hi-Tech Optoelectronic Co. Ltd.). The absorption spectra were conducted on an UNICO 2802PC spectrophotometer with a spectral window range of 350–800 nm.

2.3. Synthesis of amine-functionalized $NaYF_4:Yb^{3+}/Er^{3+}$ UCNPs

Firstly, the poly(acrylic acid) coated $NaYF_4:Yb^{3+}/Er^{3+}$ nanoparticles were synthesized before the amine functionalization. Briefly, into the mixture of ethanol (15 mL) and ethylene glycol (10 mL), the aqueous solution containing $Y(NO_3)_3 \cdot 6H_2O$ (1.7 mL, 0.5 mol/L), $Yb(NO_3)_3 \cdot 6H_2O$ (200 μL, 0.5 mol/L), and $Er(NO_3)_3 \cdot 6H_2O$ (100 μL, 0.5 mol/L) was added under stirring. The sodium fluoride solution (5.0 mL, 1.0 mol/L) and PAA (0.1 g) were then added. The white colloidal solution was subsequently transferred into a 50-mL Teflon lined autoclave and treated at 190 °C for 72 h. Then the UCNPs with bright green UC luminescence were obtained after washing and centrifugation. To make the UCNPs specifically bond with TNT, amine functionalization of the particle surface was further conducted. In a typical synthesis, the as-prepared $NaYF_4:Yb^{3+}/Er^{3+}$ UCNPs (160 mg), APTS (25 μL), EGDMA (50 μL), and AIBN (50 mg) were dispersed into the mixed solvent of acetonitrile (15 mL) and ethanol (15 mL), and then the mixture was heated at 45 °C for 6 h under stirring to form a thin layer of polymer containing APTS–EGDMA on the particle surface. The amine functionalized UC nanocrystals were washed with ethanol, collected with centrifugation, and redispersed into buffer solution ($NaOH/Na_2CO_3/NaHCO_3$, 0.02 M, pH=12) to get the stock solution with a final particle concentration of 2.2 mg/mL.

2.4. 2,4,6-Trintrotoluene (TNT) analysis

All the standard solution of the nitroaromatic were prepared by dissolving them into the mixed solvent of acetonitrile and ethanol (volume ratio=1:4) with a final concentration of 0.22 mg/mL, respectively. To conduct the TNT test, 100 μL of the as-prepared UC nanoparticle colloidal solution (2.2 mg/mL) and different amounts of TNT were mixed and formed till 1.0 mL via adding the buffer solution of $NaOH/Na_2CO_3/NaHCO_3$ (0.02 M, pH=12). The upconversion luminescence spectra of the mixture solution were measured with irradiation of 980 nm NIR light.

3. Results and discussion

The morphology and size distribution of the obtained upconversion $NaYF_4:Yb^{3+}/Er^{3+}$ nanocrystals were analyzed via the transmission electron microscope (TEM). TEM images of the upconversion $NaYF_4$ nanocrystals before (Fig. 1a) and after (Fig. 1b) functionalized with amino groups were depicted in Fig. 1. As can be seen in Fig. 1a, the nanoparticles are less than 100 nm in sizes. After amine functionalization, the morphology and size of the nanoparticles have no obvious change (Fig. 1b). However, in the high magnification TEM image of Fig. 1b, the polymer coating is visible and the thickness is less than 5 nm (Fig. 1c), indicating the successful modification with EGDMA–APTS hybrid polymer. The X-ray diffraction (XRD) pattern of the EGDMA–APTS coated UCNPs shown in Fig. 1d suggested that the NPs are hexagonal phase $NaYF_4$ (JCPDS card 16-0334) with good crystallinity. The surface coating of the $NaYF_4:Yb^{3+}/Er^{3+}$ nanocrystals was further characterized via FTIR (Fig. S1) and TGA (Fig. S2) analyses.

As a useful luminescent nanosensor for the selective detection of TNT in the mixture solution of nitroaromatics, UCNPs colloidal solution should display strong photostability. The photostability of the UCNPs colloidal solution was also investigated. Unlike the conventional organic dyes and quantum dots (QDs) which often suffer from photobleaching, these as-prepared UCNPs demonstrated a very good photostability. As shown in Fig. 2, during

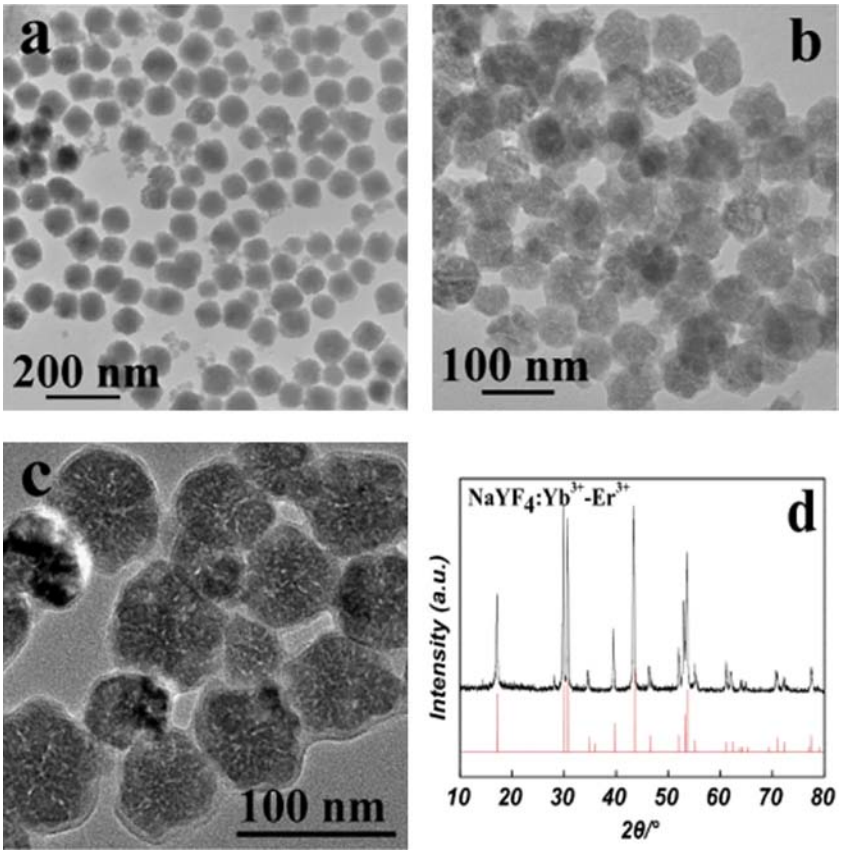


Fig. 1. TEM images of the UCNPs before (a) and after (b) coating with APTS. (c) High magnification TEM image of APTS coated UCNPs, and (d) XRD pattern of APTS coated UCNPs.

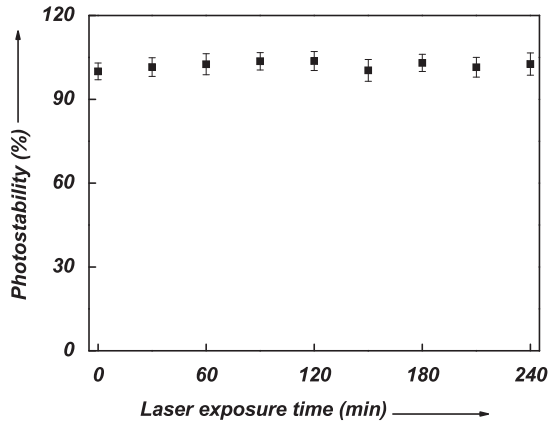


Fig. 2. Photostability tests of the UCNPs (0.22 mg/mL) colloidal solution. The laser irradiation power was 0.5 W.

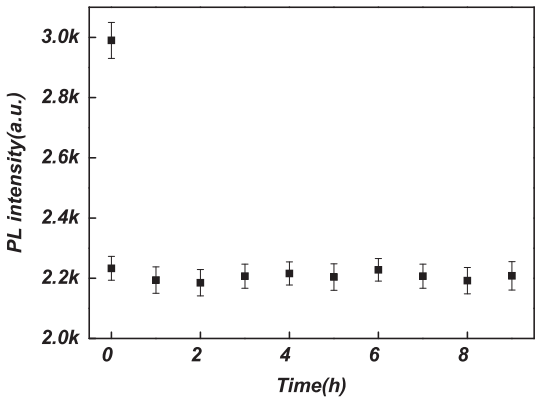


Fig. 4. Effects of incubation time on the UC luminescence quenching. UCNPs (0.22 mg/mL), TNT (3 μg/mL), room temperature, and pH=12 ($NaHCO_3$–Na_2CO_3–NaOH, 0.02 mol/L).

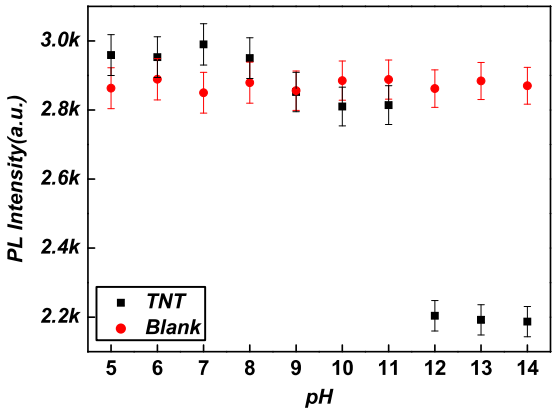


Fig. 3. pH influence on the intensity of the APTS coated UCNPs (0.22 mg/mL) before (red circles) and after (black squares) the addition of TNT (3 μg/mL). Buffer solution and concentration, pH (5): CH_3COOH–CH_3COONa (0.02 mol/L); pH (6–8): NaH_2PO_4–Na_2HPO_4 (0.02 mol/L); and pH (9–12): $NaHCO_3$–Na_2CO_3–NaOH (0.02 mol/L). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

continuous irradiation for as long as 4 h by focusing the 980-nm diode laser point on the same part of the solution, only ca. 3.7% of fluctuation rather than quenching in the UC emission intensity (543 nm) was observed (Fig. 2). It should be mentioned that this fluctuation could be attributed to the excitation instability of the diode laser after operation for a long period of time. These results indicate that the as-prepared UCNPs are extraordinarily water-stable and highly resistant to photobleaching.

Due to their good water-stability and photostability, these UCNPs are highly desirable for analytical applications as luminescent nanosensors for TNT detection. As we know, TNT is an electron-deficient Lewis acid and the methyl group of TNT can be deprotonated by the amine groups (Lewis base) to form a TNT anion [6,8,56]. The anion–cation pair (TNT–RNH^{3+}) can be decomposed by using an acidic solvent, so the pH value affects dramatically the charge transfer and further luminescence intensity. So, the pH effects on the green upconversion luminescence of APTS functionalized UCNPs before and after the addition of TNT were investigated in a wide pH range of 5–14. As can be seen from Fig. 3, before adding TNT into the UCNPs colloidal solution, the UC luminescence intensity was almost unchanged in the tested pH range. After the addition of TNT (3.0 μg/mL), the UC luminescence intensity had no obvious change in the pH range of 5–8, and decreased slightly by increasing the pH value up to 11. Under strong basic condition (pH=12–14), however, the green UC emission was quenched greatly and then kept stable, suggesting that the charge transfer has taken place at this pH value. So, the UC luminescence detection of TNT was carried out at pH=12.

To make sure that the luminescence quenching was completely in response to the analyte (TNT), the influence of incubation time on the UC luminescence intensity was further examined. The plot of response kinetics was demonstrated by checking the green UC luminescence intensity of the UCNPs colloidal solution that was incubated with TNT for a different period of time. As shown in Fig. 4, the UC luminescence of the UCNPs colloidal solution (0.22 mg/mL) was dramatically quenched as soon as the TNT (3 μg/mL) was added at pH=12 at room temperature, and the UC luminescence kept stable for over at least 9 h. So, the TNT detection was conducted at room temperature and the UC luminescence intensity was checked after the TNT was mixed with the UCNPs colloidal solution.

Due to the efficient quenching on the green UC luminescence of the APTS functionalized $NaYF_4$:Yb^{3+}/Er^{3+} nanocrystals by TNT, these UCNPs were successfully applied to the rapid, sensitive and selective luminescence quantification of TNT in the mixture solution of nitroaromatics without preconcentration, purification, and any expensive instruments. As depicted in Fig. 5, with the increase of TNT concentration, the green UC luminescence centered at 543 nm decreased step by step. Accordingly, the relative UC luminescence intensity is in negative proportion to the concentration of TNT in the range of 0.01–9.0 μg/mL with a 3σ limit of detection (LOD) of 9.7 ng/mL (inset of Fig. 5). The linear regression equation is $I=2988.4-125.7C$ ($n=7$) with the correlation coefficient of 0.9997. Herein, the I is the relative UC luminescence intensity and C is the concentration of TNT (μg/mL). As can be seen in the digital photos in Fig. 5, the colloidal solution of the APTS functionalized UCNPs is milky white in daylight and emit naked-eye visible green UC luminescence under the 980 nm irradiation. After the addition of TNT, the color of the colloidal solution in daylight is deep red because the TNT–amine complex absorbs the green part of visible light. Under the 980 nm irradiation, the green UC luminescence of the UCNPs was dramatically quenched. Compared to TNT, the addition of other three nitroaromatics including TNP, DNT, and NB has no influence on the green UC luminescence of the UCNPs. The evolution of upconversion luminescence spectra with increasing DNT, NB and TNP concentration, respectively, has been shown in Fig. S3. To confirm their highly selective recognition ability in aqueous media, other three nitroaromatics including DNT, NB, and TNP were analyzed with the as-developed method. Although all the three nitroaromatics have pretty similar chemical structures as compared with TNT (all chemical structures are shown in Fig. 6), the UC luminescence of

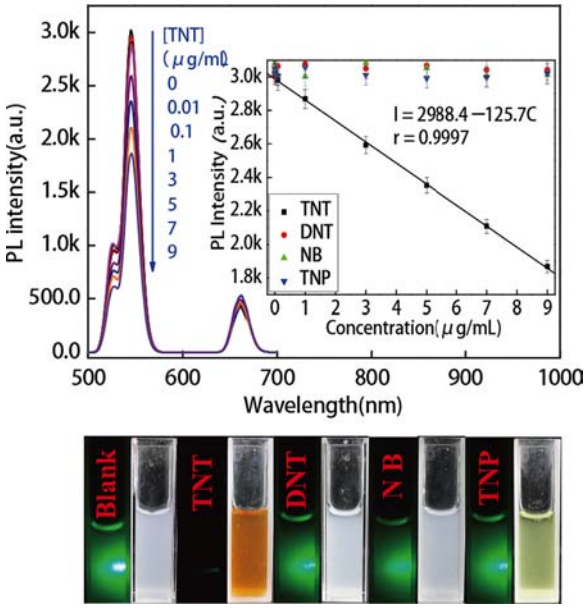


Fig. 5. Evolution of upconversion luminescence spectra with increasing TNT concentration. Inset: calibration curve and selectivity for TNT quantification. UCNPs: 0.22 mg/mL; pH=12; and $\lambda_{em}/\lambda_{em}$=980 nm/543 nm. The digital photographs show the colors of the APTS functionalized UCNPs colloidal solution (1.1 mg/mL) in the presence of different nitroaromatics (9.0 μg/mL) under irradiation (980 nm) and daylight, respectively. pH=12. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

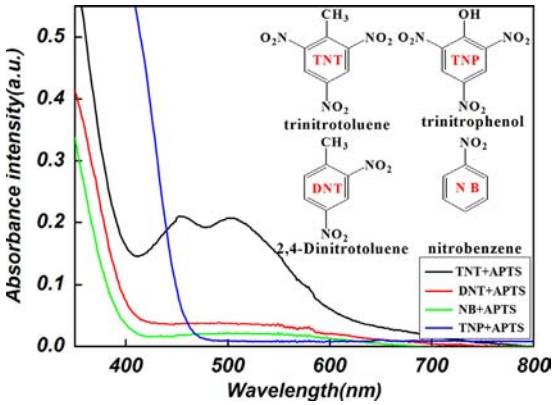


Fig. 6. The UV–vis absorption spectra of the four nitroaromatics (TNT, DNT, NB and TNP) solution (3.0 μg/mL × 2.0 mL) in the presence of APTS (2.5 μL). Solvent: buffer solution (pH=12; $NaHCO_3$–Na_2CO_3–NaOH, 0.02 mol/L). Inset: chemical structures of the nitroaromatics.

the $NaYF_4$ nanocrystals was hardly changed by these nitroaromatics. Therefore, the as-developed method can be used for the highly selective detection of trace TNT in the mixture of nitroaromatics independent of immunoassay and molecularly imprinted technology and any complicated instruments.

The mechanism of selective luminescence quenching has also been investigated. The absorption spectra of the nitroaromatics (3 μg/mL) dissolved in buffer solution (pH=12; $NaHCO_3$–Na_2CO_3–NaOH, 0.02 mol/L) were carried out in the presence of APTS (2.5 μL), respectively (Fig. 6). As shown in Fig. 6, all the nitroaromatics have a strong absorption before 400 nm. Meanwhile, the absorption of TNP red shifted to 470 nm. Because of the strong absorption before 400 nm, all the four kinds of nitroaromatics will quench the fluorescence of organic dyes and QDs used for TNT fluorescence detection when the excitation wavelength is less than 400 nm, and thus it is not easy to get rid of the interference of coexisting nitroaromatics. Please, note besides the absorption

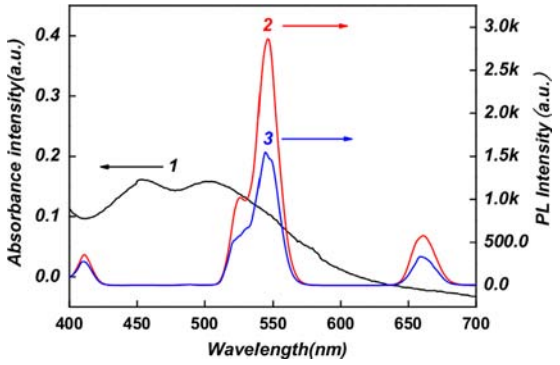


Fig. 7. Absorption spectra (1) of TNT solution (3.0 μg/mL × 2.0 mL) with addition of APTS (2.5 μL) and emission (2 and 3) spectra of the APTS functionalized UCNPs colloidal solution (0.22 mg/mL) before (2) and after (3) the addition of TNT (9.0 μg/mL).

Table 1
Analytical results for the detection of TNT in mixed samples.[a]

Sample	Concentration (μg/mL)		Recovery (%)
	Taken	Found (mean, n=6)	
TNT	3.0	2.98 ± 0.07	99.3 ± 1.11
TNT/DNT	3.0/30.0	2.96 ± 0.08	98.7 ± 1.13
TNT/NB	3.0/30.0	2.97 ± 0.09	99.0 ± 1.13
TNT/TNP	3.0/30.0	3.08 ± 0.12	102.7 ± 1.16
TNT/DNT/NB/TNP	3.0/30.0/30.0/30.0	3.07 ± 0.11	102.3 ± 1.14

[a] n is the repetitive measurement number.

before 400 nm, a wide and obvious absorption band (400–650 nm) with two peaks at 453 and 504 nm was observed in the UV–vis spectrum of TNT–APTS solution; however, other three nitroaromatics have no absorption in this range. This phenomenon can be attributed to the formation of an APTS–TNT complex in strong basic aqueous solution by the strong charge-transfer interaction, which has been proved by the absorption spectrum of TNT in the absence of APTS (Fig. S4, Supplementary material). As shown in Fig. S4, no absorption in the range of 400–650 nm was observed for the TNT in the absence of APTS. The absorption spectra of other nitroaromatics such as TNP, DNT and NB have no difference in the presence and absence of APTS. Meanwhile, the emission spectra of the UCNPs colloidal solution before and after the addition of TNT were carried out. As shown in Fig. 7, compared to the emission spectra of the as-prepared UCNPs solution without TNT (Fig. 7, spectrum 2), the peak position (543 nm) of the emission spectrum has no obvious change, but the luminescence intensity decreases greatly after the addition of TNT (Fig. 7, spectrum 3). The dramatic decrease of the emission intensity can be attributed to the obvious absorption of TNT anions (Fig. 7, spectrum 1). Therefore, the high selectivity of the as-developed TNT detection method can be attributed to the efficient energy transfer from the UCNPs to TNT instead of other nitroaromatics.

To further investigate the selectivity and applicability of this new assay method, TNT in water samples mixed with other nitroaromatics was analyzed via this strategy. In brief, the standard TNT solution (3.0 μg/mL) with various concentrations of other explosives such as DNT, NB, and TNP (30.0 μg/mL) was mixed with the as-prepared upconversion nanomaterials. Thereafter the UC luminescence intensity of the solution was checked under the 980 nm irradiation and the concentration of TNT in the mixture was deduced. As shown in Table 1, the values found for TNT in the mixture are identical with the expected ones and no obvious influence was observed, suggesting a very good selectivity. The comparison of our nanosensor and traditional methods has

been shown in Table S1. The results indicate that our method has a good selectivity for TNT analysis although the limit of detection is not pretty low. We also detected our method in real water samples and the analytical results for the determination of trace TNT have been shown in Table S2. The results show a good recovery and potential applicability of this facile UC luminescence nanosensor for TNT in real samples.

4. Conclusions

In summary, we developed a facile and novel strategy for the fabrication of upconversion luminescence nanosensor for the selective detection of TNT in the mixture solution of nitroaromatics. Different from the fluorescent dyes and QDs-based fluorescent TNT sensors in which the excitation was usually absorbed by the nitroaromatics including TNT, TNP, DNT, and NB, the upconversion emission rather than excitation of the upconverting luminescent nanosensors was absorbed only by TNT, and thus a good selectivity was obtained. Especially, this novel strategy can selectively detect TNT in the presence of TNP independent of immunoassay or molecularly imprinted technology and complicated instruments. This sensitive and selective UCNPs nanosensor allows a simple and low cost protocol for the detection of TNT in aqueous solution. The finding highlights the unique capability of the upconversion luminescent $NaYF_4$ as novel materials over the traditional fluorescent sensors for a specific application. The novel optical properties of these upconverting nanomaterials, such as good photostability, low-energy excitation (NIR light) with little damage to analytes and deep penetration, and no autofluorescence interference, should make them particularly useful for further in vitro and in vivo luminescent analysis applications.

Acknowledgments

This research was supported in part by the National Natural Science Foundation of China (21275015 and 21075009), the State Key Project of Fundamental Research of China (2011CB932403 and 2011CBA00503), the Program for New Century Excellent Talents in University of China (NCET-10-0213), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.12.009.

References

[1] Y. Engel, R. Elnathan, A. Pevzner, G. Davidi, E. Flaxer, F. Patolsky, Angew. Chem. Int. Ed. 49 (2010) 6830–6835.
[2] J. Li, C.E. Kendig, E.E. Nesterov, J. Am. Chem. Soc. 129 (2007) 15911–15918.
[3] S.S.R. Dasary, A.K. Singh, D. Senapati, H.T. Yu, P.C. Ray, J. Am. Chem. Soc. 131 (2009) 13806–13812.
[4] D.M. Gao, Z.P. Zhang, M.H. Wu, C.G. Xie, G.J. Guan, D.P. Wang, J. Am. Chem. Soc. 129 (2007) 7859–7866.
[5] G.P. Anderson, S.C. Moreira, P.T. Charles, I.L. Medintz, E.R. Goldman, M. Zeinali, C.R. Taitt, Anal. Chem. 78 (2006) 2279–2285.
[6] K. Zhang, H.B. Zhou, Q.S. Mei, S.H. Wang, G.J. Guan, R.Y. Liu, J. Zhang, Z.P. Zhang, J. Am. Chem. Soc. 133 (2011) 8424–8427.
[7] R. Batlle, H. Carlsson, P. Tollback, A. Colmsjo, C. Crescenzi, Anal. Chem. 75 (2003) 3137–3144.
[8] D.M. Gao, Z.Y. Wang, B.H. Liu, L. Ni, M.H. Wu, Z.P. Zhang, Anal. Chem. 80 (2008) 8545–8553.
[9] R.Y. Tu, B.H. Liu, Z.Y. Wang, D.M. Gao, F. Wang, Q.L. Fang, Z.P. Zhang, Anal. Chem. 80 (2008) 3458–3465.
[10] C.G. Xie, B.H. Liu, Z.Y. Wang, D.M. Gao, G.J. Guan, Z.P. Zhang, Anal. Chem. 80 (2008) 437–443.
[11] H.B. Zhou, Z.P. Zhang, C.L. Jiang, G.J. Guan, K. Zhang, Q.S. Mei, R.Y. Liu, S.H. Wang, Anal. Chem. 83 (2011) 6913–6917.
[12] E.R. Goldman, I.L. Medintz, J.L. Whitley, A. Hayhurst, A.R. Clapp, H.T. Uyeda, J.R. Deschamps, M.E. Lassman, H. Mattoussi, J. Am. Chem. Soc. 127 (2005) 6744–6751.
[13] R. Li, Y.P. Yuan, L.G. Qiu, W. Zhang, J.F. Zhu, Small 8 (2012) 225–230.
[14] M. Berg, J. Bolotin, T.B. Hofstetter, Anal. Chem. 79 (2007) 2386–2393.
[15] G. Bunte, J. Hurttlen, H. Pontius, K. Hartlieb, H. Krause, Anal. Chim. Acta 591 (2007) 49–56.
[16] M. Cerruti, J. Jaworski, D. Raorane, C. Zueger, J. Varadarajan, C. Carraro, S.W. Lee, R. Maboudian, A. Majumdar, Anal. Chem. 81 (2009) 4192–4199.
[17] J.M. Conder, T.W. La Point, G.R. Lotufo, J.A. Steevens, Environ. Sci. Technol. 37 (2003) 1625–1632.
[18] I. Cotte-Rodriguez, Z. Takats, N. Talaty, H.W. Chen, R.G. Cooks, Anal. Chem. 77 (2005) 6755–6764.
[19] C.A. Groom, A. Halasz, L. Paquet, S. Thiboutot, G. Ampleman, J. Hawari, J. Chromatogr. A 1072 (2005) 73–82.
[20] Y. Jiang, H. Zhao, N. Zhu, Y. Lin, P. Yu, L. Mao, Angew. Chem. Int. Ed. 47 (2008) 8601–8604.
[21] J.V. Goodpaster, V.L. McGuffin, Anal. Chem. 73 (2001) 2004–2011.
[22] H.R. Nie, Y. Zhao, M. Zhang, Y.G. Ma, M. Baumgarten, K. Mullen, Chem. Commun. 47 (2011) 1234–1236.
[23] D.A. Olley, E.J. Wren, G. Vamvounis, M.J. Fernee, X. Wang, P.L. Burn, P. Meredith, P.E. Shaw, Chem. Mat. 23 (2011) 789–794.
[24] R.C. Stringer, S. Gangopadhyay, S.A. Grant, Anal. Chem. 82 (2010) 4015–4019.
[25] Y.S. Xia, L. Song, C.Q. Zhu, Anal. Chem. 83 (2011) 1401–1407.
[26] T. Alizadeh, M. Zare, M.R. Ganjali, P. Norouzi, B. Tavana, Biosens. Bioelectron. 25 (2010) 1166–1172.
[27] G.P. Anderson, E.R. Goldman, J. Immunol. Methods 339 (2008) 47–54.
[28] R.G. Smith, N. D'Souza, S. Nicklin, Analyst 133 (2008) 571–584.
[29] Y.X. Ma, H. Li, S. Peng, L.Y. Wang, Anal. Chem. 84 (2012) 8415–8421.
[30] N.N. Tu, L.Y. Wang, Chem. Commun. 49 (2013) 6319–6321.
[31] H. Li, L.Y. Wang, Analyst 138 (2013) 1589–1595.
[32] L.Y. Wang, Y.D. Li, Chem. Commun. (2006) 2557–2559.
[33] L.Y. Wang, R.X. Yan, Z.Y. Hao, L. Wang, J.H. Zeng, H. Bao, X. Wang, Q. Peng, Y.D. Li, Angew. Chem. Int. Ed. 44 (2005) 6054–6057.
[34] S. Huang, M. Bai, L.Y. Wang, Sci. Rep. 3 (2013) 2023–2028.
[35] H. Li, L.Y. Wang, Chin. Sci. Bull. 58 (2013) 4051–4056.
[36] M.Y. An, J.B. Cui, Q. He, L.Y. Wang, J. Mater. Chem. B 1 (2013) 1333–1339.
[37] M.L. Deng, N. Tu, F. Bai, L.Y. Wang, Chem. Mater. 24 (2012) 2592–2597.
[38] M.L. Deng, Y.X. Ma, S. Huang, G.F. Hu, L.Y. Wang, Nano Res. 4 (2011) 685–694.
[39] L.Y. Wang, Y. Zhang, Y.Y. Zhu, Nano Res. 3 (2010) 317–325.
[40] L.Y. Wang, Y.D. Li, Nano Lett. 6 (2006) 1645–1649.
[41] T.Y. Cao, Y. Yang, Y.A. Gao, J. Zhou, Z.Q. Li, F.Y. Li, Biomaterials 32 (2011) 2959–2968.
[42] R. Kumar, M. Nyk, T.Y. Ohulchanskyy, C.A. Flask, P.N. Prasad, Adv. Funct. Mater. 19 (2009) 853–859.
[43] M. Wang, W. Hou, C.C. Mi, W.X. Wang, Z.R. Xu, H.H. Teng, C.B. Mao, S.K. Xu, Anal. Chem. 81 (2009) 8783–8789.
[44] D.K. Chatteriee, A.J. Rufalhah, Y. Zhang, Biomaterials 29 (2008) 937–943.
[45] Q. Liu, J.J. Peng, L.N. Sun, F.Y. Li, ACS Nano 5 (2011) 8040–8048.
[46] J.C. Zhou, Z.L. Yang, W. Dong, R.J. Tang, L.D. Sun, C.H. Yan, Biomaterials 32 (2011) 9059–9067.
[47] A. Xia, M. Chen, Y. Gao, D.M. Wu, W. Feng, F.Y. Li, Biomaterials 33 (2012) 5394–5405.
[48] T.S. Yang, Y. Sun, Q. Liu, W. Feng, P.Y. Yang, F.Y. Li, Biomaterials 33 (2012) 3733–3742.
[49] J.C. Boyer, F. Vetrone, L.A. Cuccia, J.A. Capobianco, J. Am. Chem. Soc. 128 (2006) 7444–7445.
[50] A. Xia, Y. Gao, J. Zhou, C.Y. Li, T.S. Yang, D.M. Wu, L.M. Wu, F.Y. Li, Biomaterials 32 (2011) 7200–7208.
[51] F. Wang, X.G. Liu, J. Am. Chem. Soc. 130 (2008) 5642–5643.
[52] L.Y. Wang, Y.D. Li, Chem. Mater. 19 (2007) 727–734.
[53] G.F. Wang, Q. Peng, Y.D. Li, J. Am. Chem. Soc. 131 (2009) 14200–14201.
[54] X. Liang, X. Wang, J. Zhuang, Q. Peng, Y.D. Li, Inorg. Chem. 46 (2007) 6050–6055.
[55] X. Liang, X. Wang, J. Zhuang, Q. Peng, Y.D. Li, Adv. Funct. Mater. 17 (2007) 2757–2765.
[56] J.L. Geng, P. Liu, B.H. Liu, G.J. Guan, Z.P. Zhang, M.Y. Han, Chem. Eur. J. 16 (2010) 3720–3727.