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

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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 $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ 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 $\mu\text{g}/\text{mL}$ 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.

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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

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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 $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ 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 $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ 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 $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ 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.

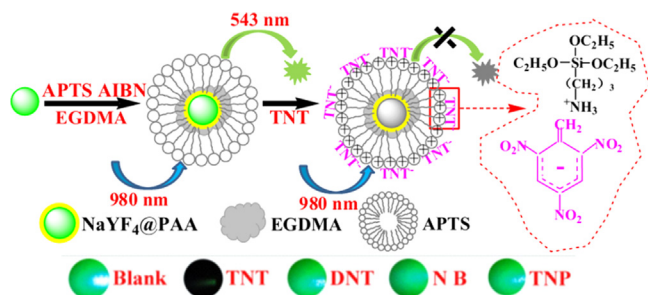
2. Experimental section

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. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (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 $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.5418 \text{ \AA}$. 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 a UNICO 2802PC spectrophotometer with a spectral window range of 350–800 nm.



Scheme 1. Scheme for the fabrication of upconversion $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ 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 $\mu\text{g}/\text{mL}$) 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.

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