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Fabrication of L-cysteine-capped CdTe quantum dots based ratiometric fluorescence nanosensor for onsite visual determination of trace TNT explosive

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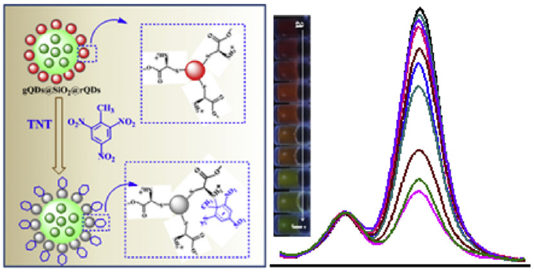
HIGHLIGHTS

- A facile strategy for preparing Lcys-capped rQDs based hybrid spheres was reported.
- Lcys serves as the stabilizer of rQDs and primary amine provider to react with TNT.
- One can perform onsite visual determination of TNT by using such probe.
- The nanosensor exhibited a wide linear range and a low detection limit.
- This sensing strategy can be fully integrated in a filter paper-based assay for TNT.

GRAPHICAL ABSTRACT



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ABSTRACT

New strategies for onsite determination of trace 2,4,6-trinitrotoluene (TNT) explosives have become a research hotspot for homeland security needs against terrorism and environmental concerns. Herein, we designed a ratiometric fluorescence nanohybrid comprising 3-mercaptopropionic acid-capped green-emitting CdTe quantum dots (gQDs) encapsulated into SiO_2 sphere and L-cysteine (Lcys)-capped red-emitting CdTe QDs (rQDs) conjugated onto SiO_2 surface. The surface Lcys can be used as not only the stabilizer of the rQDs but also the primary amine provider which can react with TNT to form Meisenheimer complexes. Without any additional surface modification procedure, the fluorescence of rQDs equipped with Lcys was selectively quenched by TNT because electrons of the rQDs transferred to TNT molecules due to the formation of Meisenheimer complexes. Meanwhile, the embedded gQDs always remained constant. Upon exposure to increasing amounts of TNT, the fluorescence of rQDs could be gradually quenched and consequently the logarithm of the dual emission intensity ratios exhibited a good linear negative correlation with TNT concentration over a range of 10 nM–8 μM with a low detection limit of 3.3 nM. One can perform onsite visual determination of TNT with high resolution because the ratiometric fluorescence nanosensing system exhibited obvious fluorescence color changes. This sensing strategy has been successfully applied in real samples and already integrated in a filter paper-based assay, which enables potential fields use application featuring easy handling and cost-effectiveness.

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1. Introduction

2,4,6-Trinitrotoluene (TNT), one of the most commonly used explosives, has been extensively used in military and industrial fields [1,2]. Moreover, TNT is a bioaccumulative and highly toxic species. The unjustified use of it leads to its release into soil, groundwater and even the food chain [3,4], making people encounter several health problems such as anemia, hepatic damage, cataract development and cancer [5]. Common methods for detecting TNT are mainly performed off-site and involve complex instrumentations such as gas chromatography [6,7], high performance liquid chromatography [8,9], mass spectrometry [10], surface enhanced Raman spectroscopy [11,12], and surface plasmon resonance spectroscopy [13,14]. Most of these techniques are sensitive and effective, but the requirements of frequent instrument calibration, lengthy and tedious operation procedures restrict their application in onsite analysis [15].

In recent years, fluorescence based sensors that utilize sensitive signal change induced by TNT have also been investigated intensively due to their merits of high sensitivity and simple operation, in combination with some smart materials, e.g., conjugated polymers [16,17], organic dyes [18,19], and semiconductor quantum dots (QDs) [20–22]. Among them, semiconductor QDs have attracted considerable attentions mainly because they offer overwhelming advantages when compared with conventional organic fluorophores and allow the easy modification of functional groups on their surfaces [21]. For example, Wang's group reported that the fluorescence of oleic-acid-covered CdSe QDs could be efficiently quenched by nitroaromatic explosives and their relative compounds [23]. After that, amino ligand-modified Mn^{2+}-doped ZnS QDs have been explored to detect TNT with a limit of detection (LOD) down to 50 nM [24]. CdTe QDs with an amine-capping L-cysteine (Lcys) layer have also been introduced to detect TNT in aqueous solution and soil samples [25]. However, most of these nanosensors are simply based on single-wavelength fluorescence changes which tend to suffer interference from adverse factors including the probe molecule concentration, excitation intensity, instrumental efficiency, and environmental conditions. Consequently, these sensors cannot provide good opportunities for visual TNT detection [26].

Ratiometric fluorescence sensors, calculation of the fluorescence intensity ratio at two different emission wavelengths, have attracted significant attention currently [27]. This technique exhibits improved sensitivity and accuracy mainly because it can eliminate a variety of effects on fluorescence signals and consequently provides greater precision to target analysis [28]. This sort of sensors have been demonstrated as vital naked eye visual sensing platforms and widely applied for the detection of various targets such as ions, protein, DNA, and so on [29–32]. Till date, most of the ratiometric fluorescence sensors are designed on the basis of organic dyes and therefore suffer from disadvantages such as a tedious synthetic process and cumbersome purification steps [33]. As an alternative, Wang's group has developed a hybrid nanoparticle-based ratiometric fluorescence nanosensor comprising of dual-emissive CdTe QDs for visual detection of TNT particulates on different package materials [34]. More recently, Lian's group has successfully developed a novel Co^{2+} doped ZnS QDs-based ratiometric fluorescence nanosensor for selectively sensing and imaging TNT in water [33]. The Lcys stabilizer capped on the doped ZnS QDs was reported to bind with TNT, resulting in aggregation of inter-dots through the formation of Meisenheimer complexes [33]. These developed nanosensors featuring high sensitivity, simplicity, and onsite TNT determination are of great significance especially heightened by current security concerns. However, more efficient ratiometric fluorescence sensors towards onsite determination of trace TNT residues are still challenging and in great demand.

Herein, we have designed a novel ratiometric fluorescence probe comprising 3-mercaptopropionic acid (MPA)-capped green-emitting CdTe QDs (gQDs) embedded into SiO_2 sphere and Lcys-capped red-emitting CdTe QDs (rQDs) conjugated onto SiO_2 surface. The Lcys layer can be used as not only the stabilizer of the rQDs but also the primary amine provider which could react with TNT to form Meisenheimer complexes. This feature allowed the fluorescence of rQDs to be selectively quenched by TNT whereas the interior emission ascribing to the gQDs remained insensitive to TNT. After exposing to different contents of TNT, the sensing system displayed continuously changed color to be easily realized by the naked eye.

2. Experimental

2.1. Reagents

3-Aminopropyltriethoxysilane (APTS), tetraethylorthosilicate (TEOS), MPA, and poly (diallyldimethylammonium chloride) (PDDA), chiorpyrifos, ochratoxinA, fumonisin B1, glucose, glycine, and catechol were obtained from Sigma-Aldrich. $CdCl_2•2.5H_2O$, Lcys ($\geq$98.5%), and tellurium powder (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). TNT, 2,4,6-trinitrophenol (TNP), 2,6-dinitrophenol (DNP), and nitrotoluene (NT) were purchased from Tianjin Chemical Reagent Plant (Tianjin, China). Double-distilled water was used throughout our study.

2.2. Apparatus

UV–vis absorption spectra were obtained from a UV-2450 spectrophotometer (Shimadzu, Japan). Fourier transform infrared (FTIR) spectra were recorded with Nicolet Nexus 470 FTIR spectrophotometer (Thermo Nicolet, USA). The transmission electron microscopy (TEM) images were received from a JEOL 2100 TEM (JEOL, Japan) performed at 200 kV. Fluorescence spectra were gained on a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan). Zeta potential was measured using a Malvern Zetasizer Nano ZS instrument (UK).

2.3. Preparation of Lcys-capped rQDs

Firstly, 63.8 mg of tellurium powder, 44.9 mg of $NaBH_4$, and 4 mL of water were transferred to a flask. This solution was bubbled with N_2 for at least 15 min and then put in the refrigerator for 3 h to obtain NaHTe solution. Secondly, 114.2 mg of $CdCl_2•2.5H_2O$ and 206.0 mg of Lcys were dissolved in 50 mL of N_2-saturated water in a 250 mL three-necked flask. The solution pH was then adjusted to 9.0 by using 2.0 M NaOH, followed by the injection of 2.5 mL of the freshly prepared NaHTe solution under vigorous stirring. After refluxing at 100 °C for 12 h, the resulting rQDs were purified and redispersed in 10 mL water for later use. These Lcys-capped rQDs are stable in solution for at least 3 months. The Lcys-capped gQDs could be obtained by the same procedure but with a refluxing time of 2 h, however, they could be stable in solution for only 2 or 3 days which made their practical use impossible. As an alternative, MPA-capped gQDs (Supporting Information) with good stability were prepared in order to fabricate the dual-emission hybrid probe.

2.4. Preparation of the MPA-capped gQDs dopped SiO_2 nanospheres

The MPA-capped gQDs dopped SiO_2 ($gQDs@SiO_2$) nanoparticles were prepared by utilizing a modified Stöber method [35,36].