



## 8-Hydroxyquinoline functionalized ZnS nanoparticles capped with amine groups: A fluorescent nanosensor for the facile and sensitive detection of TNT through fluorescence resonance energy transfer

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### ARTICLE INFO

#### Article history:

Received 27 September 2012

Received in revised form

22 November 2012

Accepted 24 November 2012

Available online 14 December 2012

#### Keywords:

ZnS nanoparticles

Surface functionalization

8-Hydroxyquinoline

Fluorescence

TNT detection

FRET

### ABSTRACT

8-Hydroxyquinolines (HQs) functionalized ZnS nanoparticles (NPs) with an amine-capping layer (ZnS–NH<sub>2</sub>–Q NPs) were prepared by a ligand-exchange process. FT-IR, XRD, NMR, TEM and fluorescence spectrometer were used to characterize the novel ZnS–NH<sub>2</sub>–Q NPs. Upon the addition of 2,4,6-trinitrotoluene (TNT), the amino groups on the surface of ZnS–NH<sub>2</sub>–Q NPs can bind TNT molecule from solution by forming Meisenheimer complex. This complex absorbs the green part of visible light, and strongly suppresses the fluorescence emission of the ZnS–NH<sub>2</sub>–Q NPs through Fluorescence Resonance Energy Transfer (FRET). The observed linear fluorescence intensity response for TNT in the range of 0–1.89 μM allows the quantitative detection TNT, with a detection limit down to 10 nM.

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### 1. Introduction

2,4,6-Trinitrotoluene (TNT), as a commonly used nitro aromatic explosive, is released into the environment mainly because of military and industrial applications. TNT residues in the environment will cause severe health problems in both animals and humans, including anemia, abnormal liver function and cataract development [1–3]. Therefore, developing optosensing materials or techniques featuring high sensitivity, simplicity, on-the-spot for real-time determination of TNT in environments have been further heightened by today's security concerns [4–6]. The fluorescence technique has been widely used to detect TNT vapor or solution owing to its strongpoint of high signal output, sensitivity and simplicity [7,8]. So far many fluorescence materials, including conjugated polymers [9–13], fluorescent dyes [14–16], semiconductor nanoparticles (NPs) [17–19], anti-TNT antibodies [20–22] and hybrid-assembly formed between these materials [23–27],

were used to detect the traces of TNT. Among these materials, semiconductor NPs or Quantum Dots (QDs) have gradually been used to detect TNT because of their great photostability, size-dependent emission wavelengths and their readily manipulated optical properties by the metal cores or the introduction of dopant ions [28]. Zhang's group reported amine-capped manganese (Mn<sup>2+</sup>)-doped ZnS NPs for TNT detection through an electron transfer (ET) mechanism, with the detection limit down to 1 nM [29]. After that, Co<sup>2+</sup> or Mn<sup>2+</sup>-doped ZnS NPs and L-cysteine-capped CdTe QDs have also been used to detect TNT in solution [17,18,30–32]. Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles and Mn<sup>2+</sup>-doped ZnS nanocomposites have been used for the magnetic separation of captured ultratrace TNT in water [33]. Chen et al. has manipulated the optical properties of Ruthenium NPs by incorporating functional molecules (such as pyrene, 4-vinylbenzo-18-crown-6, histidine, etc.) onto the surface of NPs, and applied them to detect TNT and Pb<sup>2+</sup> ions [34,35].

It is well known that the semiconductor NPs such as ZnS and CdS have a great number of surface metal atoms that can coordinate with organic ligands to form stable fluorescent complexes on the surface of NPs [36]. However, among the literatures about the TNT detection, we found that the semiconductor NPs with regulated optical properties by the functional ligands was rarely reported for fluorescent

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chemosensor. Our previous research revealed that ZnS NPs were easily modified by the phenanthroline and 8-hydroxyquinoline derivatives through metal–ligand interfacial bonding interactions [37,38]. In addition, the white light emitting semiconductor nanocrystals have been successfully synthesized from 8-hydroxyquinoline-5-sulfonic acid decorated manganese doped ZnS NPs [39]. It has also been found that the metal–ligand interfacial bonding interactions can play a significant role in regulating the optical and electronic properties of NPs [40]. These novel surface-functionalized NPs exhibited steady fluorescent properties, high photoluminescence quantum yields (QYs) as compared with the conventional zinc complexes.

In this paper, we, for the first time, used the 2-mercaptoethylamine (MEA) and 8-hydroxyquinoline (HQ) co-functionalized ZnS NPs (ZnS–NH<sub>2</sub>–Q NPs) as effective chemosensor for the TNT detection in solution through Fluorescence Resonance Energy Transfer (FRET). The HQ molecules were attached to the surface of ZnS NPs in a single coordination fashion due to the steric hindrance effect of the spherical surface of NPs, which made the ZnS–NH<sub>2</sub>–Q NPs possess unique and high fluorescent properties in organic solvents as compared with the bis(8-hydroxyquinoline) zinc(II)(ZnQ<sub>2</sub>) complex. Within the present experimental context, the fluorescence response of ZnS–NH<sub>2</sub>–Q NPs was much drastic with the content variation of TNT. This is ascribed to that the organic amine ligands on the surface of ZnS NPs can bind TNT species by forming compact Meisenheimer complex (TNT-amine complex) between the electron-rich amino groups of MEA and electron-deficient TNT [41]. The TNT-amine complexes on the surface of ZnS NPs can absorb the green part of visible light (absorption with  $\lambda_{\max}$  at 519 nm) and strongly suppress the fluorescence emission of ZnS–NH<sub>2</sub>–Q NPs (emission peak at 503 nm) due to resonance energy transfer. We wish that the reported ZnS–NH<sub>2</sub>–Q NPs sensor for TNT here opens up a potential design-thought for using organic ligands functionalized semiconductor NPs as the convenient, highly efficient and inexpensive sensor materials.

## 2. Experimental

### 2.1. Materials

8-Hydroxyquinoline (HQ), 2-mercaptoethanol (ME), 2-mercaptoethylamine hydrochloride (MEA·HCl), zinc acetate dihydrate [Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O], thiourea, dimethylformamide (DMF), chloroform (CHCl<sub>3</sub>) and dimethyl sulfoxide (DMSO) were all of analytical-grade reagents and were used without further purification. 2,4,6-Trinitrotoluene (TNT) in methanol (1 mg·mL<sup>-1</sup>) were obtained from Aladdin. 2,4-Dinitrotoluene (DNT) was purchased from TCI.

### 2.2. Measurements

The morphology of NPs were characterized by high-resolution transmission electron microscopy (HRTEM) on a Philips EM-420 at a 120 kV accelerating voltage. XRD diffraction data were collected on a Siemens D-5005 X-ray diffractometer using Cu K $\alpha$  radiation. FT-IR spectra (4000–400 cm<sup>-1</sup>) were determined with KBr disks on a Magna 560 FT-IR spectrometer. The <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer in d<sub>6</sub>-DMSO. UV–vis absorption spectra were obtained using a Shimadzu UV–2550 spectrophotometer. The fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse spectrofluorometer. The photoluminescence quantum yields (QYs) and excited-state decay times were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photo counting technique.

### 2.3. Synthesis of ZnQ<sub>2</sub> complex

ZnQ<sub>2</sub> complex was synthesized according to the literature [42]. The typical synthetic process is as follow: an aqueous solution (40 mL) of zinc acetate dihydrate (0.01 mol) was added dropwise to the acetone solution (80 mL) of 8-hydroxyquinoline (0.02 mol) and triethylamine (0.02 mol) under stirring. After refluxing the mixture at 50–60 °C for 2 h, the precipitates were collected by centrifugation (6000 rpm, 10 min) and washed with acetone and deionized water for several times, respectively. At last, the product was dried in vacuum, and 0.32 g of ZnQ<sub>2</sub> as a yellow powder was obtained.

### 2.4. Synthesis of amine-capped ZnS nanoparticles (ZnS–NH<sub>2</sub> NPs)

Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O (5.5 g, 0.025 mol), ME (2.0 mL, 0.029 mol), MEA·HCl (0.86 g, 0.08 mol), 5 mL sodium hydroxide aqueous solution (16 mol/L) and thiourea (1.7 g, 0.045 mol) were dissolved in 40 mL DMF. The mixture was stirred at 150–160 °C for 10 h under nitrogen and then concentrated to 10 mL at a reduced pressure. The resulting solution was poured into a large amount of ethanol and the white precipitate was collected and thoroughly washed several times with ethanol, and then dried in vacuum.

### 2.5. Preparation of HQ functionalized ZnS–NH<sub>2</sub> nanoparticles (ZnS–NH<sub>2</sub>–Q NPs)

HQ functionalized ZnS–NH<sub>2</sub> NPs were synthesized according to the literature [38]. Typically, 1.0 g of ZnS–NH<sub>2</sub> NPs was dispersed in 2.5 mL DMF, and 0.01 g of HQ was added. The reaction solution was allowed to stir for 30 h at room temperature, and then the resulting mixture was poured into a large amount of ethanol. The precipitation was isolated by centrifugation (8000 rpm, 10 min), and purified by repeated washing/sonication/centrifugation cycles with, sequentially, ethanol, and methanol, and then dried under vacuum overnight at room temperature. Finally, 0.9 g of ZnS–NH<sub>2</sub>–Q NPs of yellowish-green powder was obtained and these particles have very good dispersibility in polar solvents such DMF and DMSO.

### 2.6. Preparation of HQ functionalized pure ZnS nanoparticles (ZnS–Q NPs)

In order to compare the effect of amino groups on the TNT detection, we have synthesized pure ZnS–Q NPs without amine-capping layer. The synthesis of ZnS NPs without amine-capping layer is consistent with that of ZnS–NH<sub>2</sub> NPs except that not adding MEA·HCl, and the synthesis of HQ functionalized ZnS NPs is also consistent with that of ZnS–NH<sub>2</sub>–Q NPs.

## 3. Results and discussion

### 3.1. Preparation and characterization of ZnS–NH<sub>2</sub>–Q NPs sensor materials

**Scheme 1** illustrates the synthetic process of ME/MEA co-capped ZnS NPs (ZnS–NH<sub>2</sub> NPs) and HQ functionalized ZnS–NH<sub>2</sub> NPs (ZnS–NH<sub>2</sub>–Q NPs). MEA and ME co-capped ZnS NPs were prepared from zinc acetate dihydrate and thiourea in dimethylformamide (DMF) in the first step. The mercapto groups of MEA and ME can tightly bind at the surface of bare ZnS NPs due to the excess of metal ions with respect to sulfide ions at the surface of NPs. HQ was later incorporated on the ZnS–NH<sub>2</sub> NPs surface through a facile ligand exchange route. Unlike the traditional bis(8-hydroxyquinoline) zinc(II) complex, HQ molecules were attached to the surface of ZnS–NH<sub>2</sub> NPs in a single coordination fashion due to the steric hindrance effect of the spherical surface of ZnS–NH<sub>2</sub> NPs.

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