



# Luminescent SiO<sub>2</sub>@Tb/guanosine 5'-monophosphate core-shell nanoscale coordination polymers for superoxide anion detection



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## ABSTRACT

It is of great significance for superoxide anion (O<sub>2</sub><sup>•-</sup>) detection due to its important role in regulation of biological function. The nanoscale coordination polymers (NCPs) core-shell nanostructures have attracted increasing interests for their nanosized-dependent properties. In this study, SiO<sub>2</sub>@Tb/guanosine 5'-monophosphate (GMP) NCPs with core-shell nanostructures was designed for O<sub>2</sub><sup>•-</sup> detection. The SiO<sub>2</sub>@Tb/GMP NCPs core-shell nanostructures were produced by using SiO<sub>2</sub> nanoparticles (NPs) as template to control their nanosize. First, Tb<sup>3+</sup> was adsorbed on the surface of SiO<sub>2</sub>NPs by coordination with -COOH of SiO<sub>2</sub>NPs. Then the Tb/GMP NCPs shells were grown along the surface of SiO<sub>2</sub>NPs. The SiO<sub>2</sub>@Tb/GMP NCPs core-shell nanostructures were characterized with scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and Zeta potential. The resulted SiO<sub>2</sub>@Tb/GMP NCPs core-shell nanostructures displayed strong Tb/GMP emission which decreased linearly with the increased O<sub>2</sub><sup>•-</sup> concentration in the range from 5.3 nM to 6.0 μM with a limit detection of 2.18 nM. And the SiO<sub>2</sub>@Tb/GMP NCPs core-shell nanostructures also exhibited good selectivity and high sensitivity in HEPES buffer at pH 7.4.

## 1. Introduction

Reactive oxygen species (ROS) are crucial substances in cells as biological regulator. Especially, they play an irreplaceable role in metabolic process [1]. ROS contain H<sub>2</sub>O<sub>2</sub>, HClO, hydroxyl radical, superoxide anions (O<sub>2</sub><sup>•-</sup>), peroxyl radical, singlet oxygen, etc [2]. Among them, as the initial substance for conversion of majority of ROS, O<sub>2</sub><sup>•-</sup> is very worth being monitored for exploring its biological functions and providing information for pathology research [3,4]. Furthermore, since the unwanted excessive O<sub>2</sub><sup>•-</sup> might be related with lots of pathological conditions such as oxidative stress, aging, atherosclerosis, inflammation, cancer and neurodegenerative disorders, etc [5–8], designing novel method with high sensitivity, selectivity and convenient operation to monitor O<sub>2</sub><sup>•-</sup> is still a challenge [9–11].

Fluorescence is a powerful technology widely being applied in preliminary basic research for bioimaging [12,13], drug delivery [14], medical diagnosis [15–17], etc. According to the previous reports, majority of efforts have been contributed to develop fluorescence molecules for O<sub>2</sub><sup>•-</sup> detection. The structure unites of those molecules reacting with O<sub>2</sub><sup>•-</sup> could be summarized as organic selenium [18], phosphates [19,20], sulfonates [21], carboxylate [22] and carbon nitrogen single bond [23,24]. For example, Tang et al. [25] designed 9-

butyltriphenyl phosphoniumacylamino-2,7-dibenzothiazolinefluorene as O<sub>2</sub><sup>•-</sup> acceptor whose fluorescence increased upon O<sub>2</sub><sup>•-</sup> oxidizing the carbon nitrogen single bond into double bond. Part of researches were focused on modifying the fluorescein or its derivatives with sulfonyl groups [21] or phosphate group [19] to decrease the initial fluorescence so that O<sub>2</sub><sup>•-</sup> might remove these groups causing fluorescence recovery [26]. However, considering the cytotoxicity, biocompatibility and experiment cost, utilizing some biomolecules to develop novel probes for O<sub>2</sub><sup>•-</sup> detection has advantages over synthetic organic compounds.

Expecting fluorescence probes, such as semiconductor quantum dots (CdTe/ZnS, CdSe) modified with O<sub>2</sub><sup>•-</sup> acceptor have also been developed [27,28]. But the quantum dots constituted with heavy metal ion might not be environmentally friendly and their potential toxicity is still the controversial topic [29,30]. In order to obtain O<sub>2</sub><sup>•-</sup> luminescence sensor combined with biomolecules to improve biocompatibility, rare earth metal ions, such as Tb<sup>3+</sup>, are suitable luminescence materials to meet the above consideration [31,32]. Tb<sup>3+</sup> has unique narrow and sharp emission spectra, long fluorescence lifetime, low toxicity and obvious distinction [33,34]. Furthermore, it displays strong coordination ability with N or O so that it could easily form nanoscale coordination polymers (NCPs) with biomolecules at room temperature

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avoiding the structure changing caused by high temperature reaction. In the previous report,  $O_2^{\cdot-}$  can oxidize guanine to 8-hydroxyguanine [35]. But guanine displays poor solubility in water and accordingly guanosine 5'-monophosphate (GMP) which contains guanine unit and phosphates as  $O_2^{\cdot-}$  acceptor and exhibits good water solubility is used. In addition, GMP can sensitize the fluorescence of  $Tb^{3+}$  [35]. It is worth noting that  $Tb/GMP$  NCPs is not uniform amorphous NCPs and it is easy to aggregate to form a polymer, resulting in an increase in volume to form precipitate. Accordingly, it is difficult to uniformly disperse it in aqueous solution, which poses certain difficulties for fluorescence analysis. Thus, the synthesis of nanoscale and uniform NCPs is of great significance. To achieve the aim, template method was utilized to control the shape and size of NCPs. The structure and size of core-shell materials can be easily adjusted to control their properties [36]. Core-shell materials can be also used as precursors to prepare hollow materials and displace the valuable covering materials by less expensive materials. Currently, hard template method is widely used for preparing core-shell materials due to the advantages of simple operation, high repetition rate, good predictability, uniform product shape and stable performance [36,37].

In this work, we synthesized a novel  $SiO_2@Tb/GMP$  NCPs core-shell nanostructures where  $SiO_2$  nanoparticles (NPs) was acted as the hard template. The luminescence of  $SiO_2@Tb/GMP$  NCPs core-shell nanostructures could be quenched by  $O_2^{\cdot-}$ . The  $SiO_2@Tb/GMP$  NCPs core-shell nanostructures as fluorescence probe showed high sensitivity and low cost and might provide reference for further study in detection of  $O_2^{\cdot-}$ .

## 2. Experimental

### 2.1. Materials

Terbium nitrate (99.99%) was purchased from Rewin Rare Earth Metal Materials Co. Ltd (Baotou, China). Guanosine 5'-monophosphate (GMP) was purchased from Sigma-Aldrich (USA). Ammonium hydroxide (25–28%) and N,N-dimethylformamide (DMF) were purchased from Xilong Chemical Co. Ltd. (Guangdong, China). N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES) was obtained from Sangon Biotech Co. Ltd. (Shanghai, China). Pyrogallol, tetraethoxysilane (TEOS), succinic anhydride, (3-aminopropyl)triethoxysilane (APTES) were purchased from Aladdin Co. Ltd (Shanghai, China). All solutions were prepared with ultrapure water, purified by a Millipore-Q system ( $18.2 M\Omega cm^{-1}$ ). HEPES buffer (100 mM) was prepared by dissolving appropriate amounts of HEPES in ultrapure water and adjusting the pH with 1.0 M NaOH. All reagents were of analytical

grade and used without further purification. In this work,  $O_2^{\cdot-}$  was generated in the process of pyrogallol autoxidation. Nitrogen gas was bubbled in all solvents before measurement.

### 2.2. Instruments

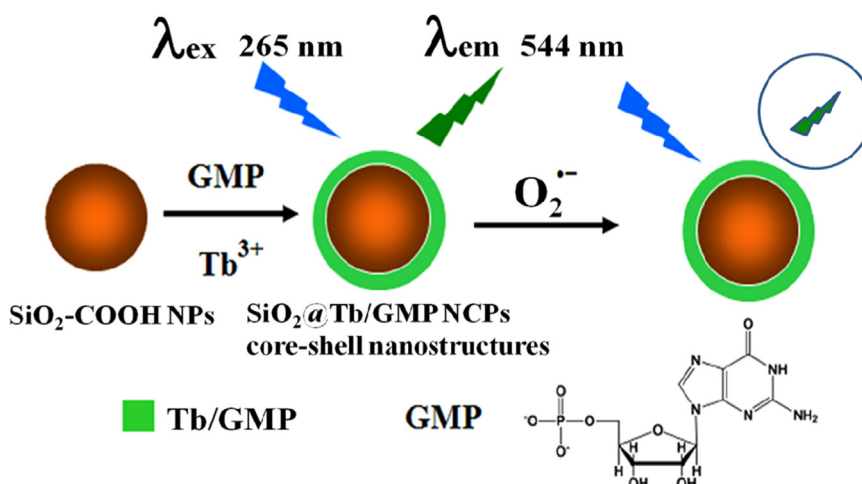
All emission spectra were observed on F-7000 fluorescent spectrophotometer (Hitachi, Japan). Fourier transform infrared spectroscopy (FTIR) was recorded on Avatar 360 FTIR spectrometer (Nicolet, USA). Transmission electron microscopy (TEM) images were taken on JEOL JEM-2100 microscopes operated at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained by using a XL30 ESEM-FEG SEM at an accelerating voltage of 20 kV equipped with a Phoenix energy dispersive X-ray analyzer. Zeta potential measurements were performed using Zetasizer nano ZS (Malvern Instruments Ltd, UA), and analysis was undertaken using 'Zetasizer software'. UV-vis absorption spectra were recorded on a Hitachi U3900 UV-vis Spectrophotometer.

### 2.3. Synthesis of $SiO_2$ NPs and $SiO_2$ -COOHNPs

The  $SiO_2$ NPs were synthesized following the previous reports [36,37]. Briefly, 15 mL ethanol was mixed with same volume of ultrapure water and ammonium hydroxide with constant stirring at 800 rpm for 30 min. Then 6 mL TEOS (diluted 10-fold with ethanol) was dropped into the above mixture slowly. After reaction for 5 h, the white precipitates were obtained by centrifugation at 10,000 rpm and washed for 3 times with ethanol. Then  $SiO_2$ NPs were dried at 60 °C for 12 h. In order to obtain the carboxyl terminated  $SiO_2$ NPs ( $SiO_2$ -COOH), firstly, the mixture of 0.5 g succinic anhydride, 1 mL APTES and 40 mL DMF were kept constant stirring at 800 rpm for 3 h. Then 8 mL  $SiO_2$ NPs solution (96 mg  $SiO_2$ NPs in DMF) was adding into the mixture over night. Finally,  $SiO_2$ -COOHNPs were obtained through centrifuging and washing.

### 2.4. Synthesis of $SiO_2@Tb/GMP$ NCPs core-shell nanostructures and $Tb/GMP$ NCPs

2.4 mg  $SiO_2$ -COOHNPs were dispersed in 10 mL 1.0 mM  $Tb(NO_3)_3$  aqueous solution by ultrasound, then 10 mL 1.0 mM GMP in HEPES buffer were dropped into the mixture under constant stirring at 1200 rpm for 2 h. Then the  $SiO_2@Tb/GMP$  NCPs core-shell nanostructures were obtained by centrifuging and washing with ultrapure water for 3 times. Finally, the product was put into freeze dryer for 12 h. The obtained solid was stored at 4 °C.  $Tb/GMP$  NCPs was also



Scheme 1. Synthetic route of  $SiO_2@Tb/GMP$  NCPs core-shell nanostructures and the detection mechanism for  $O_2^{\cdot-}$ .

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