Lanthanide Molecular Species Generated Fe$_3$O$_4$@SiO$_2$-TbDPA Nanosphere for the Efficient Determination of Nitrite

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Abstract: The presence of nitrite (NO$_2^-$) in water and food leads to serious problems in public health and the environment. Therefore, it is important to develop a rapid and efficient method for the selective detection of NO$_2^-$ ions. In this work, the synthesis and characterization of magnetic Fe$_3$O$_4$@SiO$_2$-TbDPA nanoprobe have been carried out. The Fe$_3$O$_4$@SiO$_2$-TbDPA aqueous solution exhibits a strong green emission. Due to the addition of various concentrations of NO$_2^-$ (0–100 μM), the fluorescence intensity has been suppressed. The nanoprobe Fe$_3$O$_4$@SiO$_2$-TbDPA exhibits excellent selectivity and sensitivity toward NO$_2^-$ ions. Excellent linearity is obtained in the range of 5–80 μM with a detection limit of 1.03 μM. Furthermore, the presence of magnetic Fe$_3$O$_4$ nanoparticles in Fe$_3$O$_4$@SiO$_2$-TbDPA nanoparticles will also facilitate the effective separation of Fe$_3$O$_4$@SiO$_2$-TbDPA from the aqueous solution. Our proposed strategy is expected to fabricate an organic-inorganic hybrid magnetic nanomaterial and can be used as an efficient sensor. It has been shown that this new strategy has numerous advantages, such as high stability, selectivity, and simplicity of operation. It demonstrates great potential for simple and convenient NO$_2^-$ detection. It may expand to a variety of ranges in environmental monitoring and biomedical fields.

Keywords: nitrite; core-shell nanospheres; fluorescent probe

1. Introduction

Nitrite (NO$_2^-$) is an important substance that is widely distributed in the environment and food. It has been extensively used in meat preservation and processing in order to inhibit the propagation of Clostridium botulinum and to improve the flavor of meat [1]. Meanwhile, NO$_2^-$ is a well-known signaling molecule that plays a vital role in normal physiologic activities, such as hypoxia, nitric oxide homeostasis and bloodstream regulation [2]. However, excessive intake of NO$_2^-$ can lead to a variety of disorders, including intraterine spontaneous abortion, growth retardation, central nervous system congenital defects and infant methemoglobinemia [3,4]. Furthermore, the presence of NO$_2^-$ ions in synthetic urine can be employed as an indicator of urinary tract infections [5]. Because of the toxicity of NO$_2^-$ ions, the accepted maximum contaminant levels (MCL) of NO$_2^-$ ions in drinking water are regulated to be 214.2 μM by the World Health Organization (WHO) and 71.4 μM by the U.S. Environmental Protection Agency (EPA) [6]. Traditional methods for the detection of NO$_2^-$ are given as spectrophotometry, high-performance liquid chromatography, ion chromatography, gas chromatography, electrophoresis, electrochemical methods and so on [7–11]. Although these methods have considerable sensitivity and...
Detection limits, most of them require complex equipment and instruments and tedious operational procedures and skills, which lack realistic operability and make it difficult to achieve highly sensitive, selective, qualitative and quantitative detection of \( \text{NO}_2^- \) [12–14]. Fortunately, fluorescent probes have become a suitable tool for \( \text{NO}_2^- \) detection due to their easy and rapid operation, highly sensitive, highly selective, and low cost [15–17]. Therefore, the realization of preparation for efficient and reliable determination of \( \text{NO}_2^- \) will be expected.

Lanthanide ions exhibit specific luminescence properties, including high quantum efficiency, extraordinary color purity, a long lifetime, sharp emission peaks, and large Stokes shifts [18–20]. Due to these merits, lanthanide luminescent materials have been widely studied in chemical and biological sensing systems [21–23]. In recent years, the development of lanthanide luminescent fluorescent probes for guest molecule (e.g., anions, cations, biomolecules) recognition has become an emerging field [24–27]. Our group has been devoted to the preparation of lanthanide hybrid materials and sensing applications, and the rapid development for the achievement of specific lanthanide sensors has been reported [28–30]. Previously, we found a \( \text{ClO}^- \) highly selective Europium sensor based on an oxime isomerization reaction for the first time [31]. Magnetic nanomaterials are one of the most important classes of materials due to their superior properties and their wide application in science and technology [32,33]. Taking these into account, we believe that the grafting of lanthanide ions onto magnetic nanomaterials will induce effective results. At present, this has never been mentioned for the smart magnetic nanomaterial in response to \( \text{NO}_2^- \) ions.

In this study, we rationally designed and fabricated a selective and sensitive fluorescent nanoprobe, \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \), and its effective detection of \( \text{NO}_2^- \) in the water sample was explored (Figure 1). The as-prepared \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) was fully investigated by FT-IR, UV-Vis, TEM, SEM and fluorescence spectroscopy. \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) aqueous solution exhibits a strong green emission. Its fluorescent signal was decreased depending on the presence of \( \text{NO}_2^- \). \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) exhibited good selectivity and sensitivity toward \( \text{NO}_2^- \) in a 100% aqueous solution. Moreover, after detection, the magnetic-sensitive nanoprobe was separated from the aqueous solution by taking advantage of their magnetic properties. The results shed new lights on the determination process in practical environments and biomedical analysis.

![Figure 1. Schematic diagram of \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) nanoprobe for \( \text{NO}_2^- \) detection.](image-url)
2. Experimental Section

2.1. Reagents and Materials

Terbium perchlorate (Tb(ClO$_4$)$_3$·6H$_2$O) was acquired from the Shanghai Yuelong company (Shanghai, China). Ferroferric oxide (II, III) (25% in H$_2$O), ammonia solution (NH$_3$·H$_2$O, 25%), tetraethyl orthosilicate (TEOS, 99.9%) (Si$_4$H$_{20}$O$_{14}$),aminopropyltriethoxysilane (APTES, 99.9%) (C$_9$H$_{23}$NO$_3$Si), Triton X-100, 1-hexanol and 2,6-pyridinedicarboxylic acid chloride were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the other metal salts and reagents were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China) and used without second purification.

2.2. Characterization

Transmission electron microscope (TEM) images were obtained with a JEOL JEM-2100 HR transmission electron microscope. Scanning electron microscopy (SEM) images were measured by a Tescan 5136MM scanning electron microscope. FT-IR spectra of the materials were measured within the 4000–400 cm$^{-1}$ wavenumber range by using a Prestige-21 spectrometer. UV-vis spectra were recorded on an Agilent 8453 UV-visible spectrophotometer. The magnetic properties of the samples were measured at room temperature using a BHV-55 vibration sample magnetometer (VSM) with an applied field of $-5000$–$5000$ Oe. The fluorescence spectra were collected with a Hitachi-4600 fluorescence spectrophotometer.

2.3. Preparation of Fe$_3$O$_4$@SiO$_2$-NH$_2$ Nanospheres

The Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanospheres were prepared according to the literature procedure with slight modifications [33]. Briefly, 0.13 g Fe$_3$O$_4$, 18 g Triton X-100, 16 mL n-hexanol and 75 mL cyclohexane were mixed in a 250 mL glass flask with vigorous mechanical agitation; then, 4 mL deionized H$_2$O was immediately added. Subsequently, 1 mL TEOS was added to the above solution, and the mixture was stirred for 30 min. Lastly, 0.7 mL NH$_3$·H$_2$O was added to the above mixture to initiate silica polymerization, and the polymerization was allowed to proceed for 18 h. The resulting Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanospheres were washed with water and ethanol three times and then magnetically separated using a simple bar magnet. The as-prepared Fe$_3$O$_4$@SiO$_2$ nanospheres were redispersed into a 20 mL ethanol solution. Then, 0.5 mL APTES and 0.3 mL NH$_3$·H$_2$O were added. This suspension was stirred at room temperature for 12 h. The resulting Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanospheres were collected by magnetic decantation and purified by ethanol via repeated washing. Finally, the Fe$_3$O$_4$@SiO$_2$-NH$_2$ magnetic nanospheres were dried under vacuum at 60 $^\circ$C for 12 h.

2.4. Preparation of Fe$_3$O$_4$@SiO$_2$·DPA Nanospheres

In order to obtain the 2,6-Pyridinedicarboxylic acid chloride-modified Fe$_3$O$_4$@SiO$_2$, the prepared Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanospheres (0.10 g) and 2,6-pyridinedicarboxylic acid chloride (0.30 g) were suspended in anhydrous toluene (20 mL) and refluxed for 10 h under an N$_2$ atmosphere. The obtained functionalized Fe$_3$O$_4$@SiO$_2$-DPA nanospheres were washed three times with ethyl alcohol to remove excess 2,6-pyridinedicarboxylic acid chloride and then dried under vacuum at 60 $^\circ$C for 12 h.

2.5. Fabrication of Terbium Hybrid Materials (Fe$_3$O$_4$@SiO$_2$·TbDPA)

A total of 50 mg Fe$_3$O$_4$@SiO$_2$·DPA and 50 mg Tb(ClO$_4$)$_3$·6H$_2$O were dispersed in 20 mL ethanol. Then, 0.2 mL NH$_3$·H$_2$O was added, and the mixture was refluxed for 8 h. After centrifugation, the precipitate was washed with ethanol three times and dried under vacuum at 60 $^\circ$C for 12 h to yield Fe$_3$O$_4$@SiO$_2$-TbDPA nanospheres.

2.6. Optical Studies

The stock solution of 0.1 mg/mL Fe$_3$O$_4$@SiO$_2$-TbDPA and 10 mM (Na$_2$CO$_3$, Na$_2$SO$_4$, Na$_2$HPO$_4$, NaH$_2$PO$_4$, CH$_3$COONa, NaNO$_3$, NaF, NaCl, NaBr, NaI and NaNO$_2$) were prepared in deionized water, respectively. Fluorescence response of Fe$_3$O$_4$@SiO$_2$-TbDPA
toward different anions was performed by introducing 100 μM (CO$_3^{2-}$, SO$_4^{2-}$, HPO$_4^{2-}$, H$_2$PO$_4^-$, CH$_3$COO$^-$, NO$_3^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$ and NO$_2^-$) into Fe$_3$O$_4$@SiO$_2$-TbDPA (0.1 mg) aqueous solution at room temperature, respectively.

3. Results and Discussion

3.1. FT-IR Analysis

The surface functional groups of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$-NH$_2$ and Fe$_3$O$_4$@SiO$_2$-TbDPA nanospheres were studied using the FT-IR technique. As shown in Figure 2A, the strong, broad peak at about 582 cm$^{-1}$ was attributed to the stretching vibration of the Fe-O bond, indicating the formation of magnetic Fe$_3$O$_4$ nanoparticles [34–36]. The broad bands at 1634 cm$^{-1}$ and 3420 cm$^{-1}$ were attributed to the O-H bending and stretching vibrations of water molecules [37].

After surface modification, Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanospheres possessed absorption bands caused by symmetric vibration of Si-O-Si (786 cm$^{-1}$) and asymmetric vibration of Si-O-Si (1044 cm$^{-1}$) [26]. The emerging absorption bands at about 2928 cm$^{-1}$ and 2987 cm$^{-1}$ were attributed to the stretching vibrations of –CH$_2$– groups from APTES units. The results supported that the SiO$_2$-NH$_2$ layer has covered the surface of the Fe$_3$O$_4$ nanoparticle. The appearance of two bands of 1727 and 1396 cm$^{-1}$ in Fe$_3$O$_4$@SiO$_2$-TbDPA corresponded to C=O-NH and the stretching vibration of C=O [38]. The weak absorption peak at 1582 cm$^{-1}$ was assigned to the pyridine ring. The collected results indicated that the DPA molecule was successfully grafted onto the outer surface of Fe$_3$O$_4$@SiO$_2$-NH$_2$ and coordinated with a terbium ion to form Fe$_3$O$_4$@SiO$_2$-DPA hybrid materials (Figure 2B).

![Figure 2](image-url)

Figure 2. FT-IR of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$-NH$_2$ (A) and Fe$_3$O$_4$@SiO$_2$-TbDPA (B).

3.2. UV-Vis Analysis

To further evaluate the structural information of Fe$_3$O$_4$@SiO$_2$-TbDPA nanospheres, analyses of the UV-Vis spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$-NH$_2$ and Fe$_3$O$_4$@SiO$_2$-TbDPA were carried out (Figure S1). Both Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$-NH$_2$ suspension displayed a weak absorption at 383 nm, while Fe$_3$O$_4$@SiO$_2$-TbDPA in water gave rise to not only the band at 383 nm but also the new signals at 270 and 279 nm. The achieved bands were derived from 2,6-pyridinedicarboxylic acid chloride. These results verified the successful modification of the organic ligands 2,6-pyridinedicarboxylic acid chloride onto the Fe$_3$O$_4$@SiO$_2$-NH$_2$ surface.

3.3. Morphological Analysis

The morphology of the as-prepared Fe$_3$O$_4$@SiO$_2$-TbDPA hybrid material was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) simultaneously. The TEM image showed that iron oxide nanoparticles were well encapsulated in the SiO$_2$ layer (Figure 3A). The SEM graph supported that Fe$_3$O$_4$@SiO$_2$-TbDPA
hybrid materials were almost uniform, and regular spheres were found (Figure 3B). According to the analysis, the homogenous Fe₃O₄@SiO₂-TbDPA nanospheres were established.

![Figure 3. (A) TEM and (B) SEM images of Fe₃O₄@SiO₂-TbDPA.](image)

### 3.4. Magnetic Properties

Magnetic properties of Fe₃O₄, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-TbDPA nanospheres were investigated at room temperature by vibrating sample magnetometer (VSM) in the field range from −5000 to 5000 Oe (Figure 4). The magnetization curves represent the soft magnetic behavior of the ferrite samples, which is beneficial for improving EM wave absorption [39]. The values of remanent magnetization (Mr), saturation magnetization (Ms) and coercivity (Hc) at room temperature were provided in Table S1. Compared with free Fe₃O₄ NPs (0.163 emu g⁻¹), the functionalized magnetic Fe₃O₄@SiO₂-NH₂ nanospheres were lower and had a magnetization saturation value of 0.099 emu g⁻¹. Such reduction in magnetism could be mainly attributed to the non-magnetic SiO₂ layer coating on the Fe₃O₄ nanoparticles’ surface. Similarly, the saturation magnetization of the Fe₃O₄@SiO₂-TbDPA magnetic nanospheres was found to be 0.075 emu g⁻¹. After grafting DPA, the magnetic properties of Fe₃O₄@SiO₂-NH₂ were further decreased. In addition, the Hc values of the Fe₃O₄, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-TbDPA nanocomposites were 33.856, 26.332 and 18.809 Oe, respectively. The low coercivity could be ascribed to the low resonance frequency [40, 41]. Fortunately, the Fe₃O₄@SiO₂-TbDPA nanospheres were easily separable under exposure to an external magnetic field, which proved that these magnetic nanomaterials possessed excellent magnetic properties and could be used for potential applications.

![Figure 4. Magnetic hysteresis loops of the Fe₃O₄, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-TbDPA.](image)
3.5. Selective and Sensitive Detecting \( \text{NO}_2^- \)

To verify the fluorescence properties of \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \), the excitation and emission spectra were recorded. The excitation spectrum is dominated by the peaks centered at 249 nm and 290 nm, which were identified by monitoring the emission of Tb(III) ions at 546 nm (Figure S2). In its emission spectrum, the Tb(III) ion signal was evident from the appearance of linear emission bands at 495, 546, 586, and 624 nm, respectively, corresponding to the deactivation of the Tb(III) excited states \( ^5D_4 \rightarrow ^7F_6 \), \( ^5D_4 \rightarrow ^7F_5 \), \( ^5D_4 \rightarrow ^7F_4 \), and \( ^5D_4 \rightarrow ^7F_3 \) (excited wavelength at 290 nm). Under the irradiation at 254 nm UV light, its characteristic green emission was observed with the naked eye (insert photo in Figure 5). Upon the addition of various concentrations \( \text{NO}_2^- \) (0 \( \mu \text{M} \) to 100 \( \mu \text{M} \)), the fluorescence intensity of \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) gradually decreased and eventually almost disappeared (Figure 5). The fluorescence intensity variation of \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) versus the concentration of \( \text{NO}_2^- \) followed the excellent linear equation \( Y = 0.928 + 0.028X \) \((R^2 = 0.996)\) (Figure 6). The detection of limit (DL) was determined to be 1.03 \( \mu \text{M} \) according to the equation \( \text{DL} = 3 \times \text{SD/slope} \), where SD was the standard deviation of the blank sample. The calculated DL is much lower than the MCL of \( \text{NO}_2^- \) ions in drinking water permitted by WHO and EPA. The detection limit in our proposed method has been compared with various published literature (Table S2). It is believed that the magnetic \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) nanoprobes provide acceptable values in terms of detection limits and allow assays in 100% aqueous solutions [5,7,32,42–47]. Moreover, the magnetic \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) nanoprobes can be separated from the aqueous solution by taking advantage of their magnetic properties (Figure S3). The proposed method has the unique advantages of simple operation, high selectivity, high sensitivity and low cost.

![Figure 5. Emission spectra of DPA-\( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{Tb} \) (0.1 mg/mL) aqueous solution upon the addition of \( \text{NO}_2^- \) (0–100 \( \mu \text{M} \)) under 290 nm excitation. (Inset: photographs of \( \text{Fe}_3\text{O}_4@\text{SiO}_2-\text{TbDPA} \) dispersions taken before (left) and after (right) the addition of 100 \( \mu \text{M} \) \( \text{NO}_2^- \) under 254 nm UV lamp).]

Selectivity is an important index for evaluating fluorescent probes [48–50]. To explore the selectivity performance of Fe3O4@SiO2-TbDPA, we performed analogous experiments upon the addition of 100 μM of CO32−, SO42−, HPO42−, H2PO4−, AcO−, NO3−, F−, Cl−, Br− and I−. No obvious changes were detected except NO2− (Figure 7). NO2− is a selective quencher for Tb3+ luminescence. This is due to the interaction between NO2− and Tb3+, and the fluorescence quenching is attributed to the energy transfer from Tb3+ to NO2−. These results supported the selectivity of the Fe3O4@SiO2-TbDPA nanoprobe for the effective recognition of NO2− in aqueous solutions. Overall, this magnetic nanoprobe exhibited great potential in the recognition of NO2−.

Figure 6. Linearity of fluorescence intensity ratio (F0/F) of Fe3O4@SiO2-TbDPA versus NO2− ion concentration (F0 and F represent the fluorescence intensities at 546 nm in the absence and presence of nitrite, respectively).

Figure 7. Fluorescence intensity of Fe3O4@SiO2-TbDPA (0.1 mg/mL) aqueous solution at 546 nm in the presence of 100 μM (CO32−, SO42−, HPO42−, H2PO4−, AcO−, NO3−, F−, Cl−, Br−, I− and NO2−), respectively.
3.6. Detection of Nitrite Ions in Tap Water Sample

To investigate the practical applicability of the nanoprobe Fe₃O₄@SiO₂-TbDPA, we have measured the emission intensity of tap water with varied NO₂⁻ concentrations. Appropriate amounts of NO₂⁻ (5, 10, 30 and 50 µM) were added to the tap water, and the final NO₂⁻ content was measured in all samples (4.75, 10.9, 28.9 and 50.9 µM) (Table S3). The average recoveries of nitrite for all spiked samples were in the range of 96–108%, and low relative standard deviations (2.2–3.1%) were obtained, which would be sufficient for practical use. These results substantiated that the proposed determination strategy could be valuable in real samples, suggesting its possibility in the sensing field and analytical assays.

4. Conclusions

In conclusion, we have successfully designed and synthesized a novel water-dispersible Fe₃O₄@SiO₂-TbDPA inorganic-organic hybrid nanoprobe for the rapid and sensitive detection of NO₂⁻ in 100% aqueous solutions. The as-prepared nanoprobe exhibited a good linear response for NO₂⁻ concentrations from 5 µM to 80 µM with a lower limit of detection (1.03 µM). After detection, the magnetically sensitive nanoprobe Fe₃O₄@SiO₂-TbDPA could be effectively separated from the aqueous solution using its magnetic properties. Therefore, this novel nanoprobe Fe₃O₄@SiO₂-TbDPA can provide a promising way for NO₂⁻ measurements under practical conditions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27144431/s1, Figure S1: UV-Vis spectra of Fe₃O₄, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-TbDPA in aqueous solution; Figure S2: Emission spectra of Fe₃O₄@SiO₂-TbDPA (0.1 mg/mL) in aqueous solution; Figure S3: Photograph of a magnet attracting Fe₃O₄@SiO₂-TbDPA in aqueous solution; Table S1: Magnetic parameters of Fe₃O₄, Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@SiO₂-TbDPA nanocomposite; Table S2: Comparison between the current method and the reported literatures for the detection of nitrite; Table S3: Results of determination of nitrite in tap water (n = 3).

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