

A novel fluorescence turn-on sensor for Cr³⁺ based on fluorescence resonance energy transfer between gold nanoparticles and rhodamine B

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Abstract: Up to now, “Turn-on” fluorescence sensor exhibits promising potential toward the detection of heavy metal ions, anions, drugs, organic dyes, DNA, pesticides and other amino acids due to their simple, quick detection, high sensitivity and selectivity. Herein, a novel fluorescence method of detecting Cr³⁺ in an aqueous solution was described based on the fluorescence resonance energy transfer between rhodamine B and gold Nanoparticles. The fluorescence of RhB solution could be obviously quenched (“off” state) with the presence of citrate-stabilized AuNPs. However, upon addition of Cr³⁺ to AuNPs@RhB system, the fluorescence of AuNPs was recovered owing to the strong interaction between Cr³⁺ and the specific groups on the surface of citrate-stabilized AuNPs, which will lead to the aggregation of AuNPs (“on” state). At this moment, the color of the reaction solution turned to black. Under optimal conditions, the limit of detection (LOD) for Cr³⁺ was 0.95 nM (S/N = 3) with a linear range of 0.164 nM ~ 3.270 μM. Furthermore, the proposed method exhibits excellent performances, such as rapid analysis, high sensitivity, extraordinary

selectivity, easy preparation, switch-on fluorescence response and non-time consuming.

Key words: switch-on fluorescence response; gold nanoparticles; rhodamine B; Cr^{3+} ; fluorescence resonance energy transfer

1. Introduction

Recently, owing to the rapid development of industries such as textile, plastic, paper, leather and food processing, various pollutants like antibiotics, toxic dyes [1-4] and heavy metal ions were released into the ecosystem and threatened the survival of human [5-7]. Among them, heavy metal ions like trivalent chromium ion (Cr^{3+}) have received significant attention [8-10]. As we all known that chromium ion (Cr^{3+}), which is an essential trace element, plays a significant role in environment and biological process [11, 12]. This important metal ion is closely related with the physiological activities of cells such as metabolism of fats, carbohydrates and proteins [13, 14]. Nevertheless, an overdose of Cr^{3+} can cause the genotoxic effect and malignant cancer [15, 16]. Conversely, Cr^{3+} deficiency may lead to nervous system disorder, diabetes and cardiovascular diseases [17, 18]. Consequently, it is critical to develop a rapid, efficient, and highly selective analysis method to monitor of Cr^{3+} for environmental and human health.

Until now, several in vitro and in vivo analytical methods have been reported for detecting Cr^{3+} , including high-performance liquid chromatography (HPLC), atomic absorption spectrometry (AAS), ion-coupled plasma-mass spectroscopy (ICP-MS), electrochemical analysis [19], colorimetric sensor [20-21] and liquid chromatography with ultraviolet detection (LC-UV). Despite the mentioned methods were widely used in the field of food and drug analysis, they have major disadvantages such as most of them are usually require extensive sample purification, expensive instrumentation, poor interference immunity, complexity and the need for special equipment. In contrast, fluorescence analysis is a promising method for detection of Cr^{3+} due to its advantages of low-cost, real-time detection, simplicity and high sensitivity.

Interestingly, nanoparticles, especially gold nanoparticles (AuNPs) have been broadly utilized to the fields of molecular recognition, sensor [22, 23], photocatalysis [24], electrochemiluminescence (ECL) and fluorescence analysis, due to its unique advantages of instinct optical properties, extremely high extinction coefficient, strong surface plasmon resonance (SPR), and color-tunable optical properties [25-27]. Furthermore, the easy-to-modify surfaces of AuNPs have been successfully utilized as color reporters for colorimetric cartap sensing a large variety of targets. Therefore, AuNPs have been used as ideal color reporters for colorimetric sensors. At the same time, the fluorescence analysis method based on AuNPs have been widely applied in the detection of heavy metal ions, anions, proteins, organic molecules, etc [28]. For example, Zhang et al. was reported an electrochemical-based nonenzymatic detection of glucose by using dendrimer-coated AuNPs via water splitting-assisted electrocatalysis. Based on gold nanoparticles capped with ortho-hydroxybenzoic acid, Juari Santosa [29] et al. established a fast and selective colorimetric detection of Fe^{3+} . Yang et al. used the AuNPs/ TiO_2 composites for remarkably enhanced photocatalytic H_2 evolution [30]. Zhao et al. designed a simple colorimetric and fluorescent “on-off-on” dual-mode sensor based on G-CDs/AuNPs system to detect L-cys and Zinc thiazole [31]. Chen et al. proposed an ECL immunosensor based on localized surface plasmon resonance (LSPR) between AuNPs and Pdots for the determination of pancreatic cancer exosomes [32] and Qing et al. developed a urinary miRNA ultratrace detection strategy based on single-target DNA-functionalized AuNPs for the noninvasive prognosis of post-MI [33]. However, there is no report on the determination of Cr^{3+} through the change of fluorescent intensity and color based on the fluorescence resonance energy transfer between gold nanoparticles and rhodamine B.

Herein, a switch-on fluorescent sensor was described for highly selective and sensitive detection of Cr^{3+} based on recovered fluorescence intensity of AuNPs@RhB system. The sensing mechanism is illustrated in Fig.1. Firstly, the AuNPs@RhB fluorescent probe was prepared based on the fluorescence resonance energy transfer (FRET) between AuNPs and RhB, resulting the weak fluorescence emission of RhB

("off" state). Interestingly, the fluorescence of AuNPs@RhB system was recovered by Cr^{3+} , which interacted with Cr^{3+} to recover the quenched fluorescence due to the complexation between the specific groups on the surface of citrate-stabilized AuNPs and Cr^{3+} ("on" state). Thus, a rapid and strong selectivity RhB based "Turn-on" fluorescent sensor for Cr^{3+} was constructed and successfully applied to the detection of Cr^{3+} in actual samples. Finally, the simple method has advantages of safety, rapid, high efficiency sensitivity and low cost.

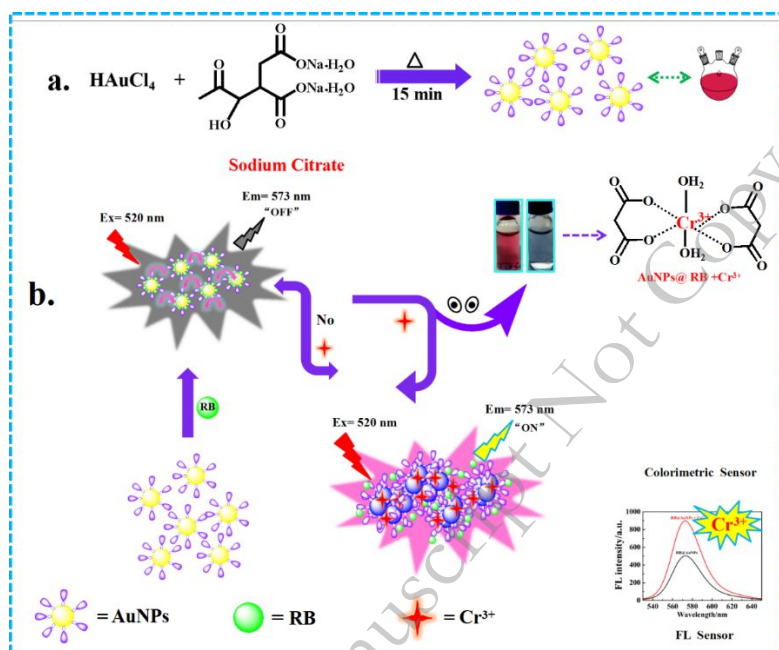


Fig.1. Schematic illustration of Cr^{3+} detection using AuNPs@RhB system as the fluorescence probe.

2. Experimental section

2.1 Materials

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$) and chromic nitrate (Cr^{3+}) were purchased from Aladdin Chemical Reagent Co. (Shanghai, China); Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 98%) was obtained from Sinopharm Chemical Reagent Co., Ltd.; Trihydroxymethylaminomethane (Tris, 98%), NaOH, KCl and other nitrates were purchased from Tianjin Kaixin Chemical Co. Ltd., (Tianjin, China). All chemicals were analytical reagent grade and used without further purification. Ultrapure water was used in all experiments.

2.2 Apparatus and Characterization

Fluorescent emission spectra were recorded on the Cary Eclipse Fluorescence Analyzer (RF-5301PC, Shimadzu Co., Japan). A UV-2450PC double-beam UV-vis spectrophotometer (Shimadzu Co., Japan) was used to record absorption spectra. FT-IR spectra were performed on a Nicolet Nexus iS50 Fourier transform infrared spectrometer (Nicolet Instrument Co. Madison, WI, USA). The pH value of the buffer solution was tested using the PHS-3B pH meter (Shanghai Instrument Co. Ltd., Shanghai, China).

2.3 Synthesis of citrate-stabilized gold nanoparticles (AuNPs)

The citrate-stabilized gold nanoparticles (AuNPs) was prepared via a simple chemical reduction process, as illustrated in Scheme 1a. In the beginning of preparation AuNPs, All the glassware must systematically cleaned with freshly prepared aqua regia (3:1, HCl : HNO₃) for about 24 h and wash carefully with double distilled water. Then the AuNPs was prepared by the reduction of HAuCl₄ with trisodium citrate (C₆H₅Na₃O₇·2H₂O) according to previous literature [34]. In brief, 1 vol% HAuCl₄ (1 mL, 10 mg·mL⁻¹) solution was added to deionized water (100 mL) and heated to boil. After that, 10 mL (38.3 mM) fresh trisodium citrate solution was rapidly poured into the boiling HAuCl₄ solution and unceasingly heated for about 15 min, followed by vigorous stirring to produce wine-red coloured solution. Finally, the gold colloidal solution was cooled to room temperature and kept in a refrigerator at 4°C before using.

2.4 Preparation of solutions

The Tris-HCl buffer solution was used to investigate the influence of pH on the measurements of Cr³⁺. Firstly, it was necessary to prepare 100 mL (0.10 M) tris solution and 100 mL (0.10 M) HCl solution. Then, the different pH values were measured by pH meter based on continuously adjusting the volume ratio of above solutions. Therefore, a pH = 6 Tris-HCl buffer solution was prepared.

2.5 Fluorescence detection of Cr³⁺

The fluorescence sensor for Cr^{3+} detection was processed at room temperature in a Tris-HCl (pH = 6) buffer solution. AuNPs (800 μL , 3 nM) was added to the solution containing RhB (1.015 mL, 1.5 μM) and Tris-HCl (1.1 mL, 0.01 M, pH = 6) buffer solution, shaking thoroughly and keeping for 2 min. Next, different concentration of Cr^{3+} were injected into the mixture. After incubation for about 4 min, the fluorescent intensity of AuNPs@RhB system in the presence (F) and absence (F_0) of Cr^{3+} were recorded at the 520 nm excitation wavelength and the 573 nm emission wavelength under the condition of 5×5 nm slit width with 530 - 650 nm wavelength scan range.

2.6 Selectivity measurements of Cr^{3+}

In the selectivity test of Cr^{3+} , various metal ions (Al^{3+} , Na^+ , Ca^{2+} , Pb^{2+} , Mg^{2+} , Ni^+ , Hg^{2+} , K^+ , Fe^{3+} , Zn^{2+} , Mn^{2+} , Cr^{6+} , Ag^+ , Cu^{2+} , Co^{2+} , Cd^{2+} , and NH_4^+) were selected as coexisting substances in the investigation of the Cr^{3+} by the AuNPs@RhB system under optimal conditions. The excitation wavelength was 520 nm and the 573 nm emission wavelength under the condition of 5×5 nm slit width with 530 - 650 nm wavelength scan range.

2.7 Fluorescence sensor detection of Cr^{3+} in real samples

To prove the detection performance of this method in practical application, the river water and tap water were centrifuged at 10000 rpm for 10 min and collected the supernatant. Then, the real samples were diluted to appropriate concentration in the detection range using ultrapure water, and stored in a refrigerator at 4°C. Subsequently, the detection of Cr^{3+} was tested by standard addition method, and the content of Cr^{3+} was determined according to the proposed method.

3. Results and discussion

3.1 Synthesis of citrate-stabilized gold nanoparticles (AuNPs)

The morphology and dispersity of the obtained AuNPs by transmission electron microscopy (TEM) were shown in Fig. 2(a-b). The results proved that the obtained AuNPs was spherical in shaped and homogeneously dispersed in aqueous solution with an average size of 13.3 nm. In addition, the optical of property of citrate-stabilized AuNPs was characterized by UV-vis absorption spectrum in the

wavelength range of 320 nm to 700 nm. As depicted in Fig. 2c, a strong characteristic surface plasmon resonance (SPR) peak around 522 nm was observed, which could be utilized to gain the concentration of AuNPs solution according to Lambert-Beer's law. According to the previous report, the extinction coefficient was $2.7 \times 10^8 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for this AuNPs. Therefore, the concentration of AuNPs solution was calculated to be 14.5 nM. In addition, the Fig. 2d was displayed the zeta potentials of AuNPs in the different pH values. The results showed that the zeta potentials were about to be -14, -18, -22.1, -26.6, -32.1 mV at pH 5.0, 6.0, 7.0, 8.0 and 9.0, respectively, which means that the zeta potential of the prepared gold nanoparticles became more negative with the increase of pH value.

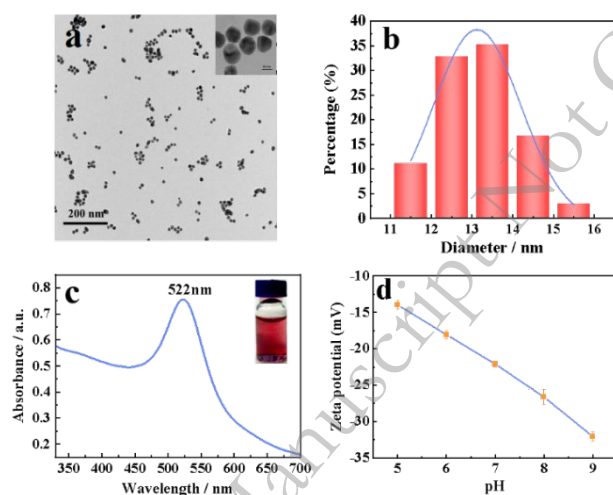


Fig. 2. TEM images (a) and size distribution (b) of AuNPs. The Absorption spectrum of AuNPs (c) and zeta potentials of AuNPs dispersed into DI water at different pH values (d).

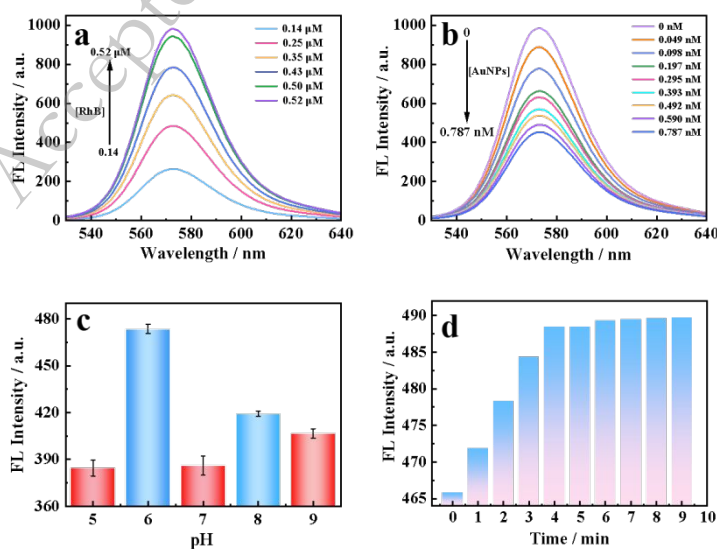


Fig.3. Fluorescence emission of RhB at different concentrations (a). and fluorescence emission of RhB in the presence of different concentrations of AuNPs (b). Effect of pH (c) and (d) reaction time on the fluorescence intensity of AuNPs@RhB system in the presence of Cr³⁺ (0.3 μM).

3.2 Optimization of detection conditions

In order to obtain high detection sensitivity, several related experimental conditions, such as the concentration of RhB, the incubation time and the medium pH value were discussed. Firstly, the concentrations of RhB played an important role for the detection of Cr³⁺ in this work. As shown in Fig. 3a, it was found that the fluorescence intensity of RhB solution trended to a maximum value when the RhB concentration was about 0.52 μM. Therefore, 0.52 μM was chosen as the typical RhB concentration in this work. More interestingly, with the increasing of AuNPs, the fluorescence intensity of RhB solution was decreased, and the minimum F value was obtained when 0.787 nM AuNPs was added to the RhB solution (Fig. 3b). Therefore, the optimal AuNPs concentration was selected as 0.787 nM in the following experiments. Additionally, the effect of the pH values of 0.1M Tris-HCl buffer solution on the fluorescence response of AuNPs@RhB system were also investigated. As shown in Fig. 3c, the fluorescence intensity of AuNPs@RhB system also changed slightly with the change of pH from 5.0 to 9.0. The maximum response was obtained at the pH = 6 of the 0.1 M Tris-HCl buffer solution. Therefore, the pH = 6 of the 0.1 M Tris-HCl buffer solution was chosen to finish assay. Afterwards, the influences of the incubation time on the Cr³⁺ detection were evaluated. As described in Fig.3d, the fluorescence intensity of AuNPs@RhB system was increased with the extension of the reaction time. As described in Fig. 3d, the fluorescence intensity of AuNPs@RhB system was almost remained the same when the incubation time reached 7 min, suggesting that the reaction time of AuNPs and Cr³⁺ reached equilibrium.

3.3 Fluorescence detection of Cr³⁺

As shown in Fig. 4(a-b), the fluorescence intensity of AuNPs@RhB system was increased with the increase of Cr³⁺ concentration. The liner relationship between the

fluorescence intensity of AuNPs@RhB system and Cr^{3+} concentration was $Y = 186.67 [\text{Cr}^{3+}] + 0.25$ ($R^2 = 0.9986$), where the F and F_0 were the fluorescence intensity of AuNPs@RhB system in the presence and absence of Cr^{3+} . Under the optimal conditions, the limit of detection (LOD) for Cr^{3+} was as low as 0.95 nM ($3\sigma/S$) with the linear region of 0.164 nM - 3.27 μM . The results showed that the advocated method was excellent for fluorescence detecting Cr^{3+} compared with other methods (As shown in Table1). Moreover, it was worth noting that the absorbance at 670 nm enhanced gradually as the Cr^{3+} concentration ranging from 0 to 640 nM in the UV-Vis absorption spectrum (Fig. 4c). And a good linear relationship was acquired between $I_{670\text{nm}} / I_{522\text{nm}}$ and Cr^{3+} concentrations (0 - 640 nM) with $R^2 = 0.9985$, where the $I_{670\text{nm}}$ and $I_{522\text{nm}}$ were the absorbance values at 670 nm and 522 nm, respectively. The LOD of Cr^{3+} could calculate to be 9.76 μM in the colorimetric methods (Fig. 4d). Moreover, the above results demonstrated that AuNPs@RhB system were suitable to be applied as a fluorescence probe for the quantitative determination of Cr^{3+} , respectively. Therefore, in the UV-vis absorption spectrum, a satisfactory linear relationship could also be obtained with the change of Cr^{3+} concentration, indicating that the proposed fluorescence sensing system could meet the quantitative determination of Cr^{3+} , and had certain practical application prospects.

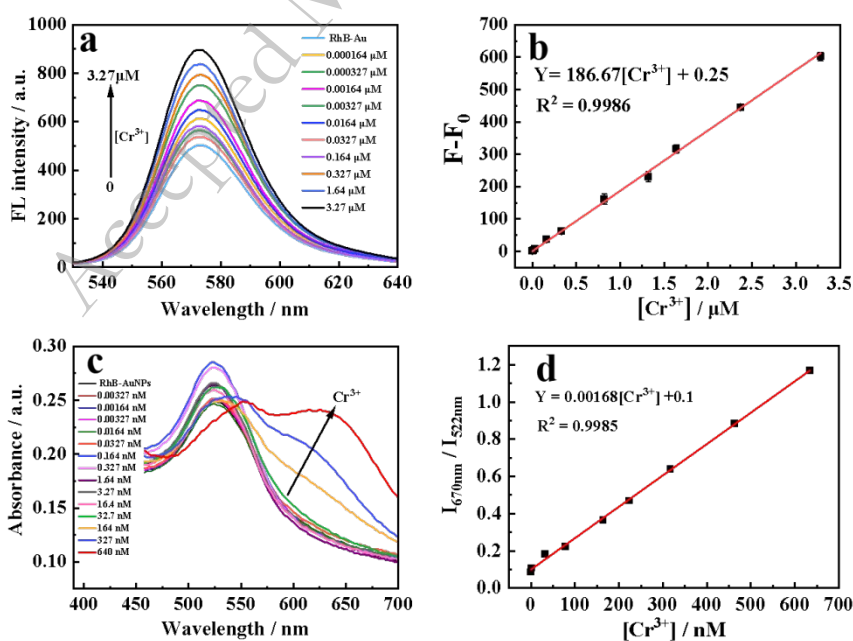


Fig. 4. Fluorescence emission spectra of AuNPs@RhB system in the presence of different Cr^{3+} concentrations (a). The fitting of linear relationships between $F-F_0$ and different concentrations of Cr^{3+} (b). The absorption spectrum of AuNPs@RhB system in the presence of different Cr^{3+} concentrations (c). The plot of $I_{670\text{nm}} / I_{522\text{nm}}$ versus Cr^{3+} concentrations (d).

3.4 Selectivity toward Cr^{3+}

Moreover, the validity and selectivity of the promoted fluorescence sensor was researched in Fig. 5. Various potential interfering agents were added into the AuNPs@RhB system under optimal conditions. Fig.5 reveals an excellent selectivity for Cr^{3+} towards other substances, such as Al^{3+} , Na^+ , Ca^{2+} , Pb^{2+} , Mg^{2+} , Ni^{2+} , Hg^{2+} , K^+ , Fe^{3+} , Zn^{2+} , Mn^{2+} , Cr^{6+} , Ag^+ , Cu^{2+} , Co^{2+} , Cd^{2+} , and NH_4^+ . As depicted in Fig. 5a, only Cr^{3+} could increase the fluorescence of AuNPs@RhB system, rather than other interfering agents, demonstrating the high selectivity of this fluorescence probe. Interestingly, the AuNPs@RhB system exhibited different color changes in the presence of different substances (insert Fig. 5a), which possibly due to the aggregation of AuNPs. In addition, to investigate the selectivity of the proposed method, the influence of some possible interfering compounds was also examined through the UV-vis spectroscopy. Based on the results obtained in Fig. 5b, there had no obvious absorbance peaks of the other interfering compounds at 522 nm compared to Cr^{3+} . The Cr^{3+} final concentration was 20 μM . And the concentrations of other interferences were about 10-fold than Cr^{3+} . Therefore, the proposed fluorescence sensing system was further verified to have high selectivity for Cr^{3+} combined with UV-Vis absorption spectra.

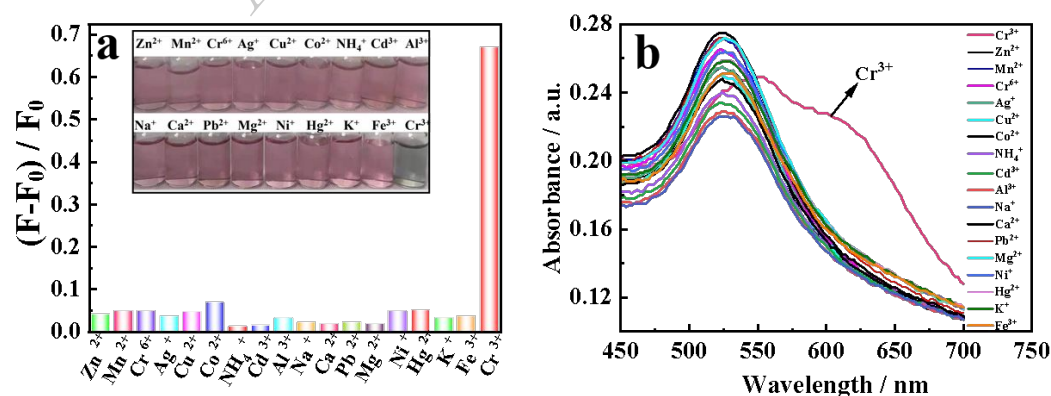


Fig. 5. Fluorescence response (a) and the absorption spectrum (b) of the AuNPs@RhB system in the presence of Cr³⁺ and other metal ions.

3.5 Detection of the Cr³⁺ in real samples

In order to prove that the proposed sensing system could be used for the detection of real samples. The fluorescence probe of AuNPs@RhB was used to determine the Cr³⁺ in river water. The content of Cr³⁺ in the actual sample was detected by the experiment of labeling and recovery. The results were summarized in Table 2. The results indicated there was a good recoveries rates (in the ranges of 90 ~ 110 %) for Cr³⁺ in river water. Hence, it was suggested that the promoted sensing system could be successfully applied to the detection of Cr³⁺ in actual samples.

4. Possible mechanism about sensing of Cr³⁺

According to the previous experiments, the fluorescence intensity of RhB solution could be intensively quenched by the as-prepared AuNPs. But it is worth noting that the fluorescence intensity of RhB solution could be obviously increased with the addition of Cr³⁺ to the AuNPs@RhB system. Therefore, to elucidate the possibility of sensing mechanism, the fluorescence spectra of RhB and the UV-vis spectra of AuNPs were taken and analyzed (Fig. 6). The UV-vis absorption spectrum of AuNPs (blue line) and the fluorescence emission spectrum (yellow line) were shown in Fig. 6. It was obvious that the fluorescence emission spectrum (yellow line) of RhB greatly overlapped with the absorption spectrum (blue line) of AuNPs to an extent, suggesting that FRET might take place between RhB (as donor) and the AuNPs (as acceptor). This phenomenon was also been proved by the decrease of the fluorescence intensity of RhB with the increase of AuNPs concentration.

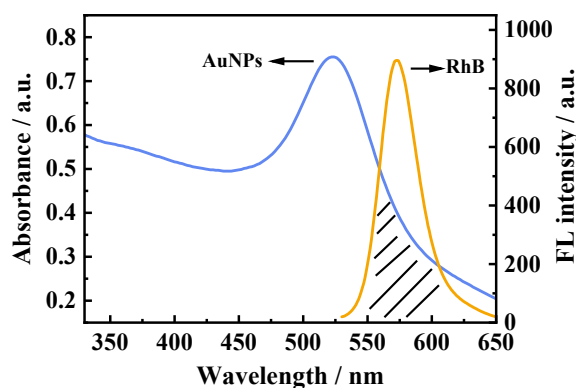


Fig. 6. Absorption spectrum of AuNPs (blue line) and fluorescence emission spectrum of RhB (yellow line).

Additionally, the TEM images of AuNPs@RhB system after adding a certain amount of Cr^{3+} were measured to investigate the reason of the recovery of the fluorescence intensity of RhB. From the Fig. 7a and Fig. 7b, the TEM images of AuNPs@RhB were exhibited a significant aggregation driven by Cr^{3+} ion. Moreover, to further prove the detection mechanism of AuNPs@RhB system for Cr^{3+} , the absorption spectrum of the AuNPs@RhB (purple line), AuNPs@RhB in the presence of Cr^{3+} (yellow line) and only Cr^{3+} (blue line) was performed in Fig. 7c. Compared with AuNPs, the spectrum of Cr^{3+} solution had a weaker adsorption peak at 575 nm. However, upon addition of Cr^{3+} , the adsorption peak of AuNPs@RhB exhibited a red-shift and appeared a new absorption peak at 670 nm. At this moment, the color of AuNPs@RhB solution immediately turned to black (Fig. 7d). Therefore, the reason for the recovery of fluorescence intensity of the proposed sensing system might be due to the strong interaction of Cr^{3+} with specific groups on the surface of citrate stabilized AuNPs, causing AuNPs to aggregate. The color of the reaction solution turned black after adding Cr^{3+} , and the fluorescence intensity of the advocated system was further restored.

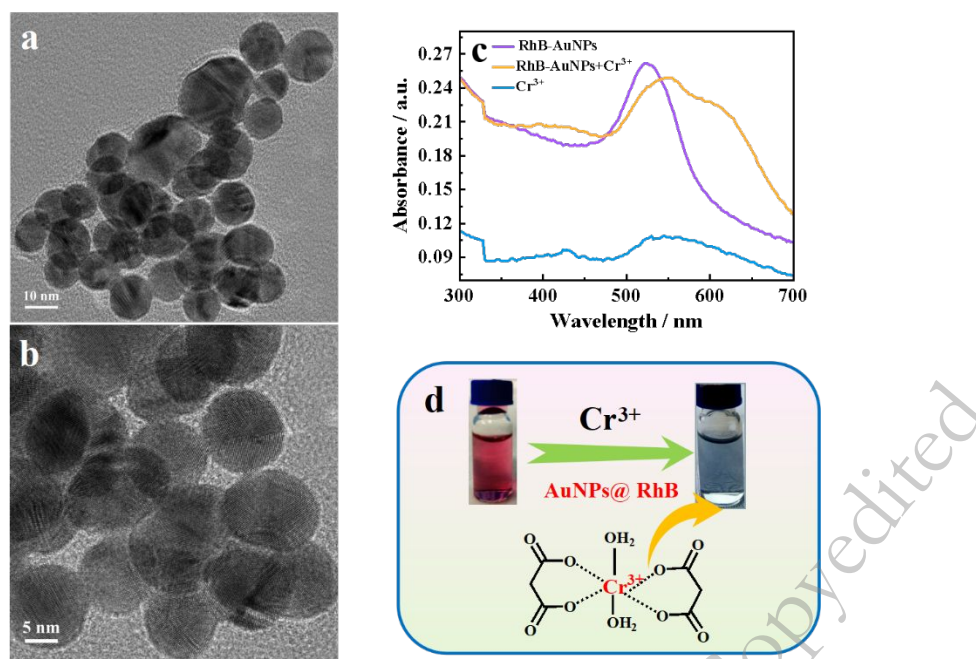


Fig.7. TEM images for AuNPs@RhB system after addition of Cr^{3+} (a, b). The absorption spectrum (c) of the AuNPs@RhB (purple line), AuNPs@RhB in the presence of Cr^{3+} (yellow line) and only Cr^{3+} (blue line), respectively (c). The possible mechanism about sensing of Cr^{3+} (d).

Table 1 Comparison of different methods for Cr^{3+} sensing

fluorescent probes	Performance		Ref.
	detection limit(nM)	linear range (μM)	
Py-An COF	81700	0-495	[35]
CdTe QDs	3.81	0.05-5	[36]
NBN-Embedded Polymers	14.69	0-25	[37]
1,2,3-triazolyl- γ -propyltriethoxysilanes	60.6	0-0.6	[38]
JXUST-2	100	0-50	[39]
Cd(II)-MOF	600	0-30	[16]
g-CNQDs	230	0.64-63	[40]
RhB@AuNPs	0.95	0.000164-3.27	this work

Table 2 Determination of Cr^{3+} in actual samples by AuNPs@RhB fluorescent probe

Sample	Added (μM)	Found (μM)	Recovery n=3 (%)
River Water	0.8	0.72	90
	1.2	1.24	103
	2.0	2.18	110

5. Conclusion

In summary, a novel fluorescence and colorimetric sensor for Cr^{3+} was proposed using AuNPs@RhB probe. Upon addition of Cr^{3+} to AuNPs@RhB system, fluorescence intensity was recovered based on the complexation between the specific groups on the surface of citrate-stabilized AuNPs and Cr^{3+} , resulting the aggregation of AuNPs. Based on the view above, the assay proved that this method displayed several advantages of high sensitivity, excellent selectivity, simplicity and non-time consuming with a detection limit of 0.95 nM. Overall, this work will open up a new insight into the application of AuNPs@RhB system in sensing Cr^{3+} in environment.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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