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SHORT REPORT

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4-Mercaptobenzoic acid-modified Au@Ag nanoparticle-based colorimetric Cr^{3+} ions detection in aqueous solution

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Abstract

Heavy metal ions pose a threat to both ecological balance and human health owing to the non-biodegradable and poisonous characteristics. A simple, convenient and rapid metal ion monitoring plays a significant role for eliminating metal ions pollution. In this work, we prepared 4-mercaptobenzoic acids (4-MBA)-functionalized silver-coated gold nanoparticles (Au@Ag NPs) as colorimetric probes to construct colorimetric Chromium III (Cr^{3+}) ions detection platform. The results showed that 4-MBA-Au@Ag NPs could effectively coordinate with the low-concentration Cr^{3+} ions with the group of -COOH, generating the obviously colorimetric reaction. To detection system, the optimal concentration of 4-MBA and pH was 5 μM and 9, respectively. Signal response was found to be proportional to Cr^{3+} ions concentration in the range from 10 to 500 μM with a correlation coefficient of 0.993, with UV–Vis and colorimetric detection limits determined as 9 μM and 10 μM, respectively. In addition, the recovery of the system was estimated to be from 88.2 to 112.1%, which was satisfactory for practical analysis of samples. The platform would have great potential applications in many areas.

Keywords Cr^{3+} ions, Au@Ag nanoparticles, 4-mercaptobenzoic acids, Detection

Introduction

Metal ions are utilized as the important cofactors for proteins with diverse functions, in electron transfer, dioxygen binding and activation (Das et al. 2016). Human beings often used specific metal ions as the trace elements to keep the normal life function (Das et al. 2016; F. AhkongSkin et al. 1994). The metal ions enter into the body via drinking water and food, and the high level in food chain might lead human being to suffer from serious diseases, such as growth disorders, severe malfunction, carcinogenesis or death (Halliwell and Gutteridge 1990; Breydo and Uversky 2011). Therefore, the effective monitoring for the metal ions in aqueous systems should be used to control water environment. Chromium III (Cr^{3+}), accumulated strongly in the food chain, was one of the most toxic heavy metal ions (Calevro et al. 1998; Breydo and Uversky 2011). Abnormal level of Cr^{3+} ions potentially causes heart failure, abdominal pain, high blood pressure, and cancer, even after a minute exposure. According to the Environment Protection Agency (EPA) guidelines, Cr^{3+} concentrations must not exceed 50 μg L^{-1} in drinking water (Liu et al. 2021; Ji et al. 2019).

Now, many approaches had been developed to determinate Cr^{3+} ions in aqueous solution accurately, such as atomic absorption spectrometry (AAS) (Sun et al. 1997; Mashhadizadeh et al. 2013), inductively coupled plasma mass spectrometry (ICP-MS) (Lichte et al. 1987; Chen et al. 2021), X-ray fluorescence spectrometry (XRF) (Borkhodoey et al. 2016; Alfred et al. 2021), and chromatography. Those methods had good sensitivity and accuracy, but some of them involve a pretreatment step

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and were thus rather time-consuming. Currently, colorimetric methods were widely developed due to the rapid responses, convenient operation and intuitive results (Ninwong et al. 2020; Yu et al. 2021; Yuan et al. 2020; Arshad et al. 2020), such as silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs). AgNPs as colorimetric sensor had significant advances of much higher extinction coefficients and lower prices compared to other nanomaterials probes (Hang et al. 2015). However, AgNPs was not stable and easily oxidized. Therefore, we synthesized the Ag@Ag NPs as probe to detect metal ions in aqueous solution. The Au@Ag NPs were more stable for synthesis and storage, more uniform and well-distributed compared with the Ag nanoparticles (Zhang et al. 2015; Shankar et al. 2012). In our work, we used 4-MBA to modify Au@Ag NPs as probe to construct the colorimetric system for metal ions detection owing to the coordination between the group of -COOH of 4-MBA and metal ions.

In our work, we employed 4-MBA to functionalize the surface of Au@Ag NPs as the colorimetric probe for the Cr^{3+} ion detections in aqueous solution due to the optical characteristic (Shankar et al. 2004). In the detection system, the 4-MBA-Au@Ag NPs with the group-COOH of the 4-MBA would coordinate Cr^{3+} ions in the aqueous solution. This would induce the aggregation of 4-MBA-Au@Ag NPs, which lead to the change of UV–Vis spectrometer and colorimetric reaction. According to the mechanism, we constructed the detection platform for colorimetric Cr^{3+} ion detection with rapid reaction, simply operation and high specificity and selectivity.

Experimental section

Materials

All chemicals used were of analytical grade. Hydrogen tetrachloroaurate hydrate ($HAuCl_4{\cdot}4H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). 4-Mercaptobenzoic acid was purchased from Tokyo Chemical Industry Co., Ltd (Japan). $Cr(NO_3)_3{\cdot}9H_2O$ and other metal ions were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Ascorbic acid (AA) was purchased from Tianjin Dingshengxin Chemical Co., Ltd. (Tianjin, China). $AgNO_3$ was purchased from Tianjin Tiangan Chemical Technology Development Co., Ltd. (Tianjin, China). Trisodium citrate (Na_3Ct) and sodium hydroxide (NaOH) were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). All water was treated through the Milli-Q purification system (18.2 MΩ cm^{-1}). UV–Vis absorption spectroscopy was recorded on a UV-2550 spectrophotometer (Shimadzu, Japan), using a 1-cm pathlength quartz cuvettes for measurements.

Preparation of 4-MBA modified Au@AgNPs

AuNPs were prepared by the chemical reduction of $HAuCl_4$. Briefly, 50 ml of $HAuCl_4$ (wt, 0.01%) aqueous solution was added to the flask and heated to boiling for 8 min, and then, 1.5 ml of sodium citrate solution (1%) was added. After 3 min of reaction, the solution turned wine red, stopped heating, and continued to stir for 30 min. AuNPs were successfully synthesized.

Then, we successively added 6 ml AuNPs, 225 μL of 0.1 M NaOH, 180 μL of 0.1 M AA and 45 μL of 0.1 M $AgNO_3$ into 24 ml aqueous water under stirring conditions. Furtherly, the above mixture was stirred for 30 min after the solution changed from wine red to orange. Au@AgNPs were successfully obtained.

The effect of the concentration of 4-MBA on the detection system was investigated, the concentration of 4-MBA was 1×10^{-7}, 1×10^{-6}, 5×10^{-6}, 1×10^{-5}, 1×10^{-4}, 1×10^{-3} M, respectively. Besides, we also studied the effect of pH on the detection system. The range of pH was from 3 to 11.

Assay for Cr^{3+} ions in aqueous solution

The UV–Vis spectrometer and colorimetric detection of Cr^{3+} in aqueous solution were performed at room temperature. Briefly, 300 μL of aqueous Cr^{3+} solutions of various concentrations was added to 2.7 mL of 4-MBA-Au@Ag NPs probes. After shaking for 30 min, the mixture of samples and detection regents was detected by UV–Vis spectrometer. Each experiment was performed in triplicate.

Specificity analysis

The specificity of probe was evaluated by determining another eight relevant metal ions, namely Hg^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Cr^{2+}, Ni^{2+}, Co^{2+}, and As^{2+}. Solutions of Zn^{2+}, Al^{3+}, Fe^{3+}, Ni^{2+}, Sr^{2+}, La^{3+}, Cu^{2+}, Ce^{3+}, Co^{2+} added to 100 μL portions of the Au@Ag NPs suspension. The other procedures of the specific experiments were the same as those for Cr^{3+} detection. Each experiment was performed in triplicate.

Results and discussion

Detection mechanism

In our work, we constructed the detection platform for colorimetric Cr^{3+} ions detection using 4-MBA-Au@Ag NPs. Compared to AuNPs and AgNPs in the detection platform, the characteristics of Au@Ag NPs were more stable with the stronger optical performance (Fig. 1) (Shankar et al. 2004). Cr^{3+} ions in the samples would be coordinated by the group -COOH residues of the 4-MBA moieties on the surface of the Au@Ag NPs. This would induce the aggregation of 4-MBA-Au@Ag NPs, which

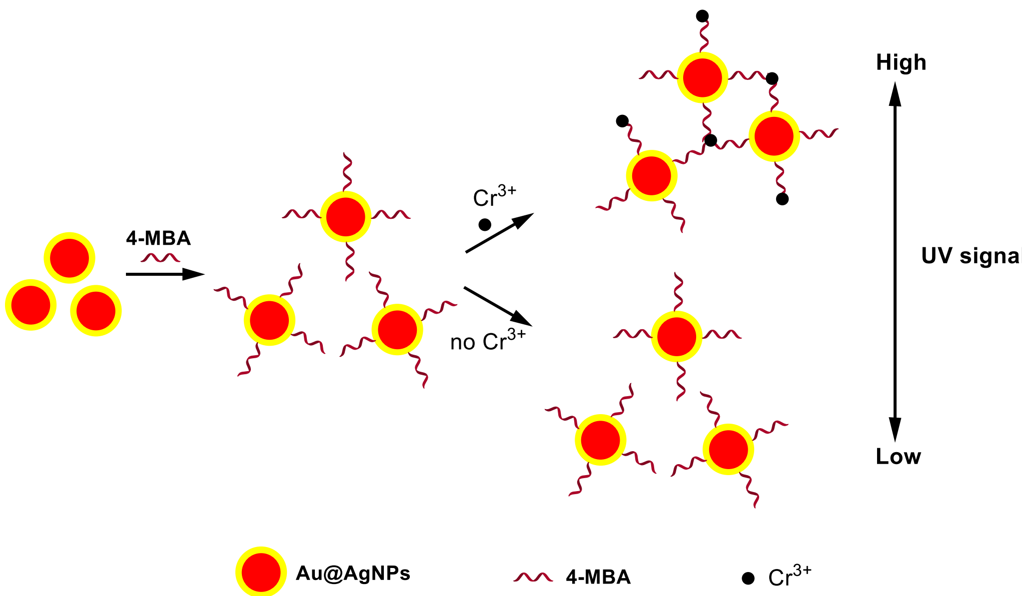

Fig. 1 Schematic illustration of the detection of Cr^{3+} ions based on the aggregation of 4-MBA-Au@Ag NPs owing to the coordination between Cr^{3+} ions and -COOH group of the 4-MBA

lead to the change of UV–Vis spectrometer and colorimetric reaction. According to the mechanism, we constructed the detection platform for Cr^{3+} ions detection.

The optimal of 4-MBA concentration

4-MBA-Au@Ag nanoparticles could capture Cr^{3+} ions via the coordination between the group of -COOH of 4-MBA and Cr^{3+} ions. So, the concentration of 4-MBA played an important role in the detection process. We firstly investigated the effect of 4-MBA concentration on the detection results (Figs. 2 and 3). The concentration of 4-MBA was 10^{-7} M, 10^{-6} M, 5×10^{-6} M, 10^{-5} M, 10^{-4} M and 10^{-3} M, respectively, and the Cr^{3+} ions were 10^{-4} M. As shown in Fig. 2a and b, there were an obvious colorimetric reaction and spectrometer changes when 4-MBA was both 5×10^{-6} M. The results showed that metal ions would coordinate with 4-MBA with different force. 4-MBA-Au@Ag NPs could react with Cr^{3+} ions when the concentration of 4-MBA was 10^{-7} M.

In addition, there was no reaction with other metal ions. Then, the colorimetric performance was enhanced with the increasing of the 4-MBA concertation. However, there was obvious reaction between other metal ions and 4-MBA when the concentration was 10^{-5} M. In order to obtain the excellent performance for the detection platform, the optimal concentration was 5×10^{-6} M.

The effect of pH on the detection system

The detection platform mainly relied on the coordination between Cr^{3+} ions and the group of –COOH of 4-MBA. The pH value had a great effect of the coordination reaction owing to the statues of the group of –COOH. So, the colorimetric reaction also depended on the pH value. We furtherly studied the effect of pH on detection system, including 3, 4, 5, 6, 7, 8, 9, 10 and 11 (Fig. 4). It can be seen that the pH value had a great effect on the UV–Vis spectrum and colorimetric image. The signals were weak between blanks and the detected samples from 3 to 5. Then, the signal gradually increased with the increasing of pH value. Meanwhile, the signal reached the plateau between blanks and the detected samples when the pH was 9. In addition, the colorimetric performance also was shown from the image in various pH values. The results showed that the detection system had a good colorimetric reaction in the condition of pH = 9. The results indicated that the optimal pH value was 9 in the detection platform.

Sensitiveness

In order to effectively detect metal ions in aqueous solution, sensitiveness for detection system is of great importance. Therefore, we evaluated the detection sensitivity of 4-MBA-Au@Ag NPs via colorimetric reaction and UV–Vis spectrum (Fig. 5). The results showed that there was a correlation curve between the Cr^{3+} ion concentration, and the ratio of the absorbance at 650 nm and 410 nm from 10 μM to 500 μM for 4-MBA-Au@Ag NPs and the R^2 was 0.993. Besides, the limit of detection can reach 9 μM.

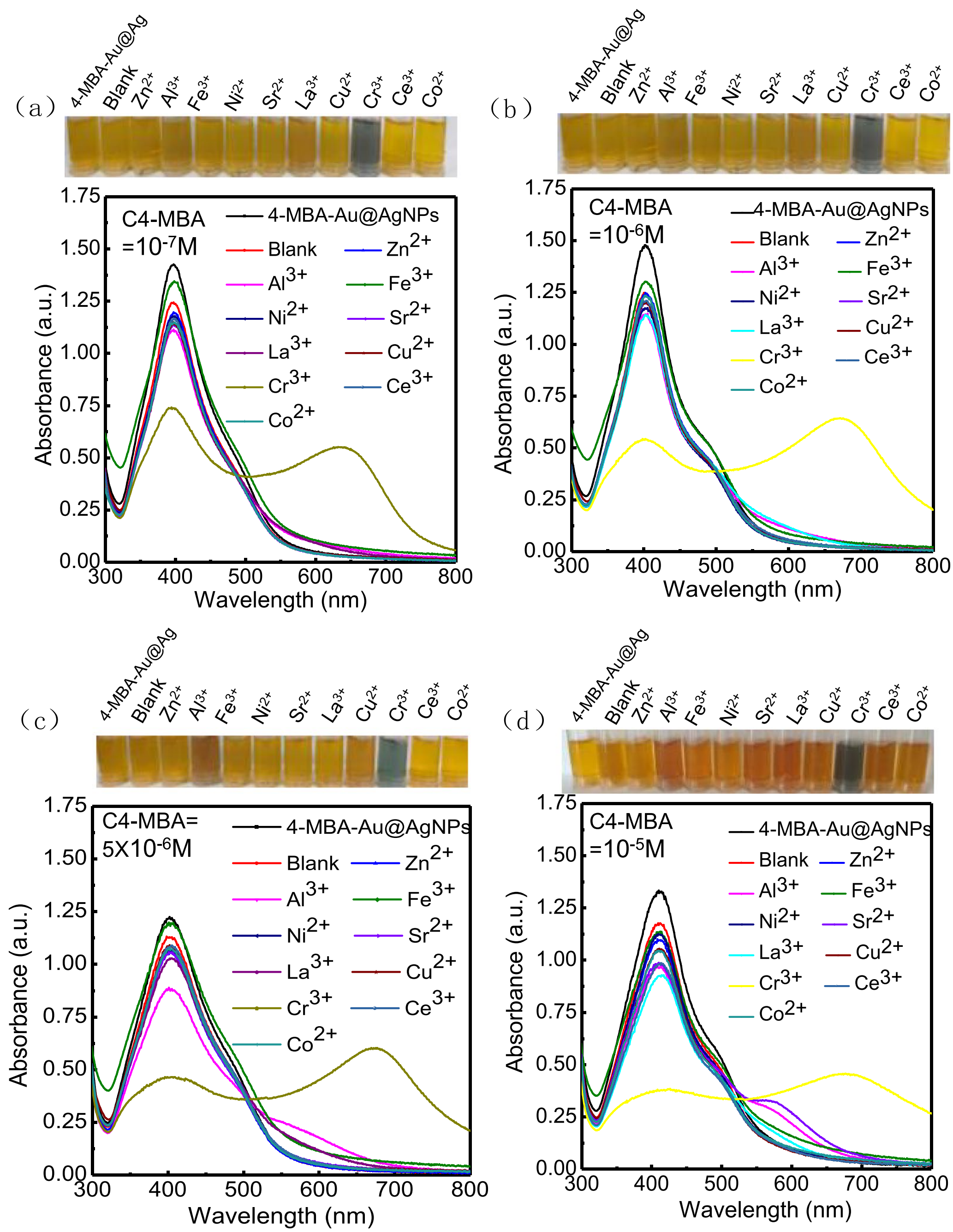

Fig. 2 The effect of 4-MBA concentration on the metal ions detection system of 4-MBA-Au@Ag NPs, including colorimetric image and UV–Vis spectrum. The concentration of metal ions was all 5×10^{-3} M, and 4-MBA concentration was 10^{-7}, 10^{-6}, 5×10^{-6}, 10^{-5} M, respectively

Selectiveness and recovery test

The composition was extremely complex in the real samples, which contained various interferents. The excellent selectiveness played an important role in detection system. So, we investigated the selectiveness and recovery to test the accuracy. Many metal ions and negative ions were chosen, and those ions might exist in the real aqueous solution. We mixed these ions with the solution of the 4-MBA-Au@Ag NPs to test the colorimetric reaction (Fig. 6). The results showed that only the exposure to Cr^{3+} ions led to the obvious signal changes, while the exposure to other tested ions does not cause any appreciable

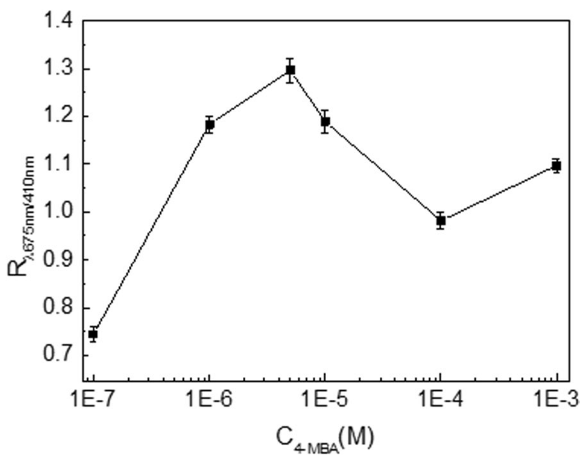

Fig. 3 The effect of 4-MBA concentration on the detection system. The concentration was 10^{-7} M, 10^{-6} M, 5×10^{-6} M, 10^{-5} M, 10^{-4} M and 10^{-3} M, respectively

change in the peak of 4-MBA-Au@Ag NPs. In addition, there was an apparent color change in 4-MBA-Au@Ag after exposure to Cr^{3+} ions, and other ions could not cause the same color changes under the same conditions. Therefore, the developed 4-MBA-Au@Ag NPs as a Cr^{3+} ions sensing system have excellent selectivity.

In addition, the recovery test of the 4-MBA-Au@Ag system was further evaluated to ensure the practicability of the developed method (Table 1). The simulated samples were prepared to perform the recovery test. All samples were spiked with Cr^{3+} ions with various concentrations. The recovery of the system was estimated to be from 88.2 to 112.1%, respectively. The recovery of the detection system is satisfactory for practical analysis of samples. All the experiments were performed in triplicate.

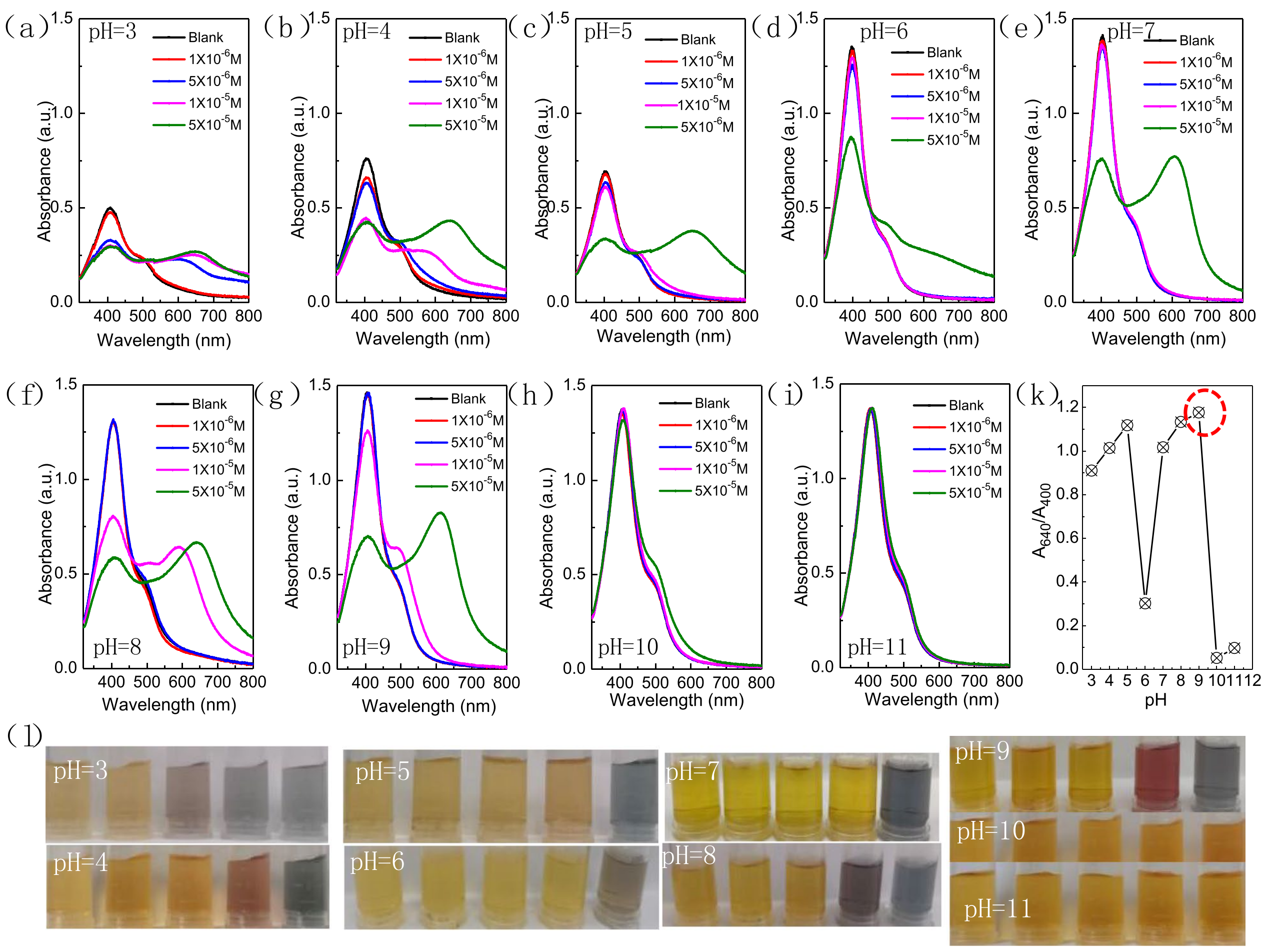

Fig. 4 The effect of pH on the detection system. The UV–Vis spectrum (**a–k**) and the image in light (**i**) for detection of metal ions with 4-MBA-Au@Ag nanoparticles

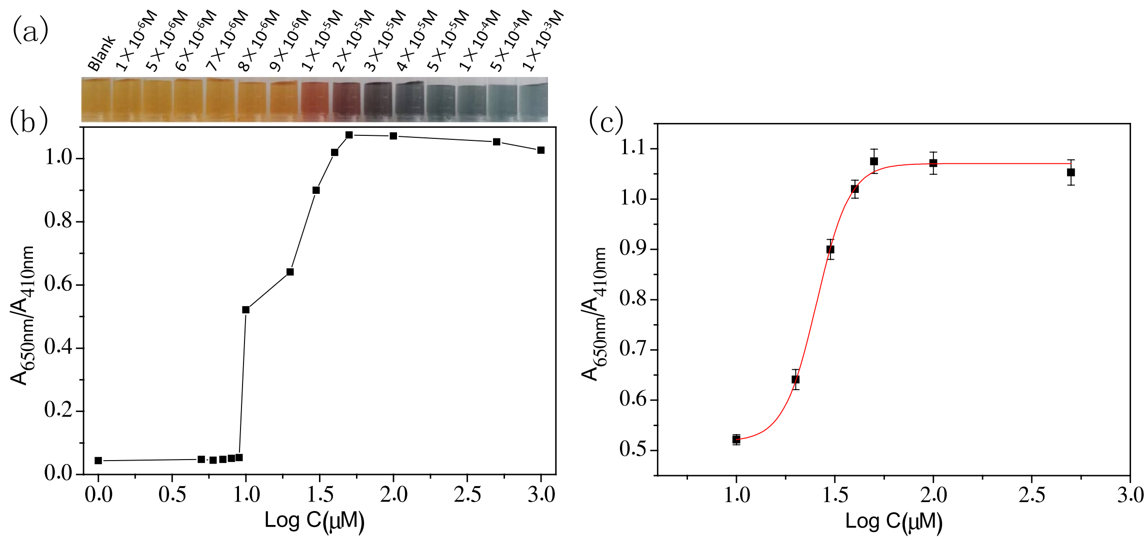

Fig. 5 Optimization of experimental conditions for Cr^{3+} ions detection with various concentrations, **a** images, **b** UV–Vis spectrum, **c** the relationship between A_{650nm}/A_{410nm} and Cr^{3+} ions concentration. The limit of detection was 9 μM and colorimetric detection of Cr^{3+} ions 10 μM. The linear range was from 10 to 500 μM

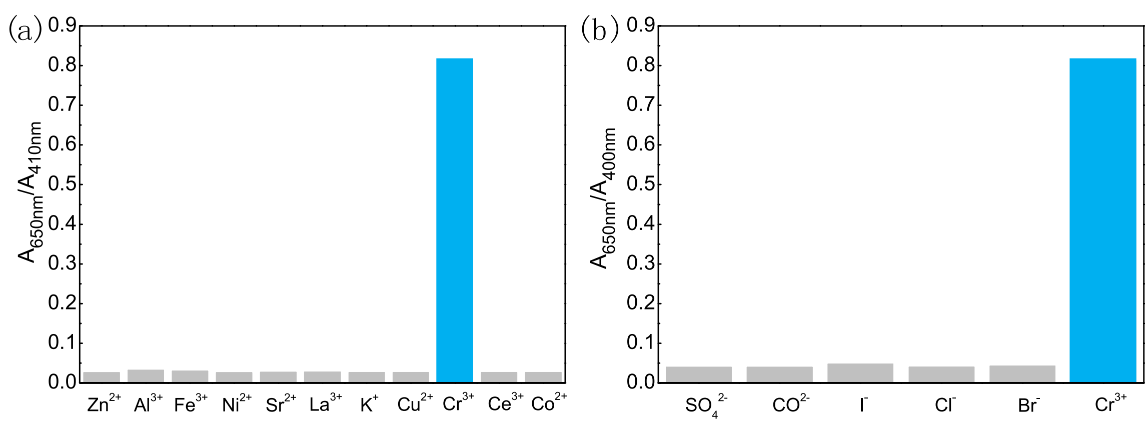

Fig. 6 The selectivity of 4-MBA-Au@Ag NPs for Cr^{3+} ions in the interferences, including other metal ions and anion

Table 1 Cr^{3+} ions were detected by 4-MBA-Au@Ag NPs in different simulated samples

Samples	Added (mM)	Founded (mM)	Recovery (%)	RSD (%)
1	15	14.67	97.8	1.2
2	25	22.04	88.2	3.5
3	28	27.1	96.8	2.8
4	33	37.00	112.1	3.5
5	38	38.92	102.4	3.0
6	40	39.90	99.8	3.8

Conclusions

In this work, 4-MBA-Au@Ag NPs were designed to colorimetric and selective Cr^{3+} ions detection in aqueous solution. The sensing strategy was based on the coordination between Cr^{3+} ions and 4-MBA and the optical characteristic of Au@Ag NPs. The optimal pH was 9 in the detection system. Cr^{3+} ions in aqueous solution can be effectively detected, and the limit of detection can reach 9 μM and 10 μM via UV–Vis and colorimetric detection. The probe was successfully used to calorimetrically detect Cr^{3+} ions with rapid reaction, simply operation and high specificity and selectivity. It might provide a potential promising method for Cr^{3+} ions detection in food safety and environment monitoring.

Abbreviations
4-MBA 4-mercaptobenzoic acids
Au@Ag NPs Silver coated gold nanoparticles
Cr3+ Chromium III

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Not applicable.

Author contributions
YML designed the experiment. ZKZ, HL and DAG carried out the experimental studies and collection, analysis, and interpretation of data. ZKZ wrote the manuscript. All authors helped to draft and revise the manuscript. All authors read and approved the final manuscript.

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Declarations

Competing interests
The authors declare that they have no competing interests.

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