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PAPER

Colorimetric detection of Cr^{3+} using tripolyphosphate modified gold nanoparticles in aqueous solutions

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A sensitive and selective colorimetric assay method for the detection of Cr^{3+} has been developed using tripolyphosphate functionalized gold nanoparticles ($\text{P}_3\text{O}_{10}^{5-}$ -AuNPs). Infrared (IR) spectra and energy dispersive X-ray spectroscopy (EDS) confirmed that tripolyphosphates capped on the surfaces of gold nanoparticles (AuNPs). Gold nanoparticles were prepared by reducing HAuCl_4 with sodium borohydride (NaBH_4) in the presence of sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$). Upon exposure to Cr^{3+} , the color of the gold nanoparticle solution changed from red to violet, which was in response to the surface plasmon absorption of dispersed and aggregated nanoparticles. The $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs were bound by Cr^{3+} and showed excellent selectivity compared to other ions (Hg^{2+} , Fe^{3+} , Cr^{6+} , Mn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Ba^{2+} , Co^{2+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Na^+ , Cl^- , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , NO_3^- , and all of the above interfering ions with the exception of Cr^{3+}) and had a detection limit of 10^{-7} M by the naked eye in this way. Most importantly, the $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs can be stored at room temperature over half a year. In addition, the $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs were also used to detect Cr^{3+} in real environmental water samples, with low interference.

Introduction

During the past decade, gold nanoparticles (AuNPs) have been widely used in a range of applications including: sensing, electronics, and surface enhanced Raman spectroscopy (SERS), as they exhibit strong surface plasmon resonance (SPR) absorption with extremely high extinction coefficients (10^8 – 10^{10} M^{-1} cm^{-1}) in the visible wavelength range.¹ The high SPR is dependent on the composition, size, and shape of the gold nanoparticles and sensitivity to the inter-particle distances. In view of this advantage, lots of colorimetric sensors have been developed for the detection of metal ions,^{2–7} proteins,⁸ oligonucleotides,⁹ and organic molecules,^{10–13} most of which can be distinguished as aggregation sensors based on cross-linking and electrostatic absorption. In these assay methods, the introduction of ligands onto the surfaces of gold nanoparticles not only stabilize AuNPs in solution, but also can interact with metal ions through a coordination reaction. Furthermore, analyte-triggered aggregation of these functionalized AuNPs leads to a red shift in the SPR absorption band resulting in a red-to-gray color change. Above all, the distance-dependent SPR absorption of AuNPs has

become a useful tool for the development of colorimetric sensing with various analytes.

It is known that trivalent chromium (Cr(III)) is an integral part of the glucose tolerance factor, and it plays an important role on the regulation of sugar and lipid metabolism. Moreover, Cr(III) can prevent certain mutations of genetic materials in cells as a nucleic acid stabilizer; thereby it can prevent the occurrence of cancer. Many cases have been reported where the complete removal of Cr(III) from the diet has caused chromium deficiency. However, larger amounts and different forms of chromium can be toxic and carcinogenic. Most importantly, as we all know Cr(III) is less harmful than hexavalent chromium (Cr(VI)), in the aqueous solution containing Cr(VI) , by adding a certain amount of reducing agent, making the solution containing only trivalent chromium, then it could be used as a useful method for detecting the content of Cr(VI) . Besides, through the determination and control the content of trivalent chromium, not only to understand the performance of the bath, the conductivity of the solution, the situation of the anode, *etc.*, but also to ensure the normal electroplating with chrome. Above all, the content of trivalent chromium is essential to the quality of electroplating chromium coatings. Nowadays, chromium has been increasingly used in a number of industrial processes including chrome plating, dye and pigment fabrication, leather tanning, and wood preserving. Due to the increasing threat of chromium exposure in the environment, there has been a growing interest in the development of highly sensitive and selective assay methods for the determination of chromium over the past few years. Various sensor systems have been reported.^{14–22} Most of these systems,

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however, have either limitations with respect to simplicity, selectivity, and time consuming for Cr^{3+} determination using voltammetric, electrothermal atomic absorption spectrometry, and surface plasmon field-enhanced resonance light scattering. Besides, the diphenylcarbazide colorimetric method is simple and fast, but certain substances react with the 1,5-diphenylcarbazide reagent to form a colored product which is absorbed at 520–540 nm that may obscure or interfere with the quantization of the chromate peak.²³ Therefore, the development of a sensor that is not only sensitive and selective but also simple and practical for Cr^{3+} determination remains a challenge.

In this report, a new strategy for the efficient recognition and detection of Cr^{3+} in the aqueous solutions through tripolyphosphate modified AuNPs has been reported. Herein, AuNPs were prepared by reducing HAuCl_4 with NaBH_4 in the presence of $\text{Na}_5\text{P}_3\text{O}_{10}$. These AuNPs have been coated with tripolyphosphates to selectively bind Cr^{3+} (Scheme 1). Also, the IR spectrum and EDS suggest that tripolyphosphates were capped on the surfaces of gold nanoparticles. In the presence of Cr^{3+} , these modified AuNPs interacted with Cr^{3+} through the cooperative metal–ligand reaction, which led to the aggregation of AuNPs quickly resulting in excellent sensitivity and high selectivity of the detection of Cr^{3+} . Moreover, the presence of Cr^{3+} can be monitored by a colorimetric response of functionalized AuNPs, and it has a detection limit of 1.0×10^{-7} M by the naked eye in this way, making it a promising rapid and sensitive technique for Cr^{3+} analysis.

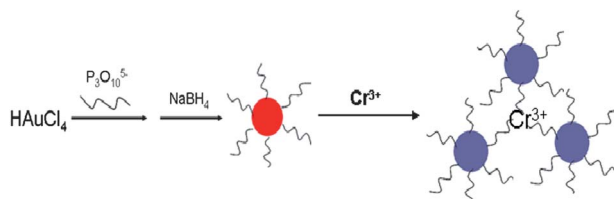
Experimental section

Materials and characterization

Hydrogen tetrachloroaurate (III) tetrahydrate and sodium borohydride were purchased from Shanghai Chemical Reagent Co. Ltd. without further purification. Sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) was obtained from Aladdin. All of the chemicals were used as received. UV-vis spectra were performed using a Lambda 950 from Perkin Elmer. Transmission electron microscopy (TEM) images and EDS data were recorded from a Tecnai F20 instrument and were operated at 200 kV. IR data were obtained on Nicolet 6700 Fourier-Transform Infrared Spectrometer. ICP-AES data were recorded on an ICP-AES Perkin-Elmer, Optima 2100.

Preparation of $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs

AuNPs were prepared by reducing HAuCl_4 with NaBH_4 in the presence of $\text{Na}_5\text{P}_3\text{O}_{10}$. All the glassware was washed with aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$ (v/v), aqua regia - prepare



Scheme 1 An analytical process for Cr^{3+} detection using tripolyphosphate modified gold nanoparticles.

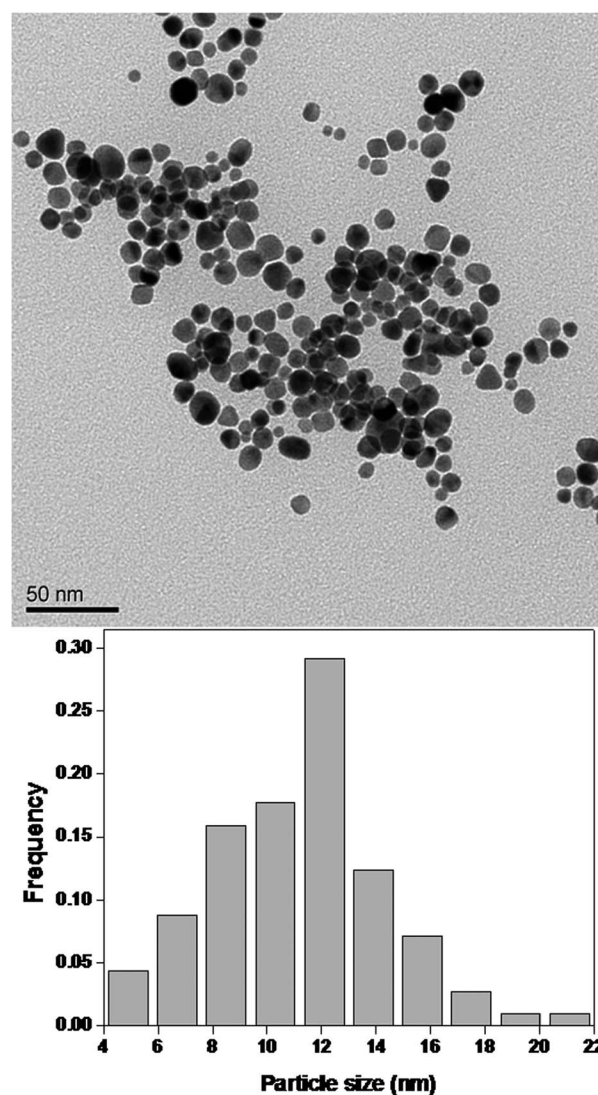


Fig. 1 (Top) A typical TEM image and (bottom) histogram of particle size distribution of $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs.

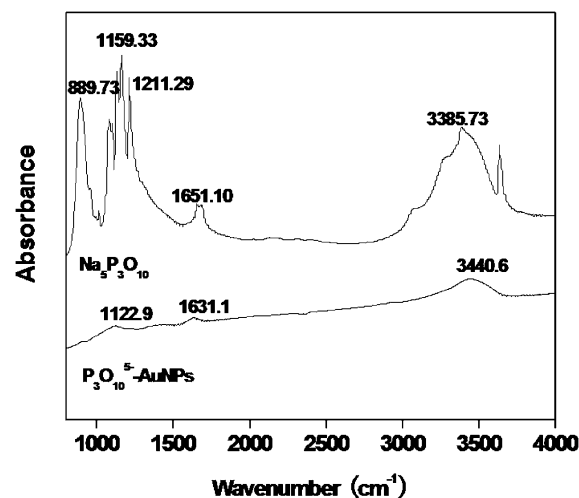


Fig. 2 IR spectra of $\text{Na}_5\text{P}_3\text{O}_{10}$ and $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs.

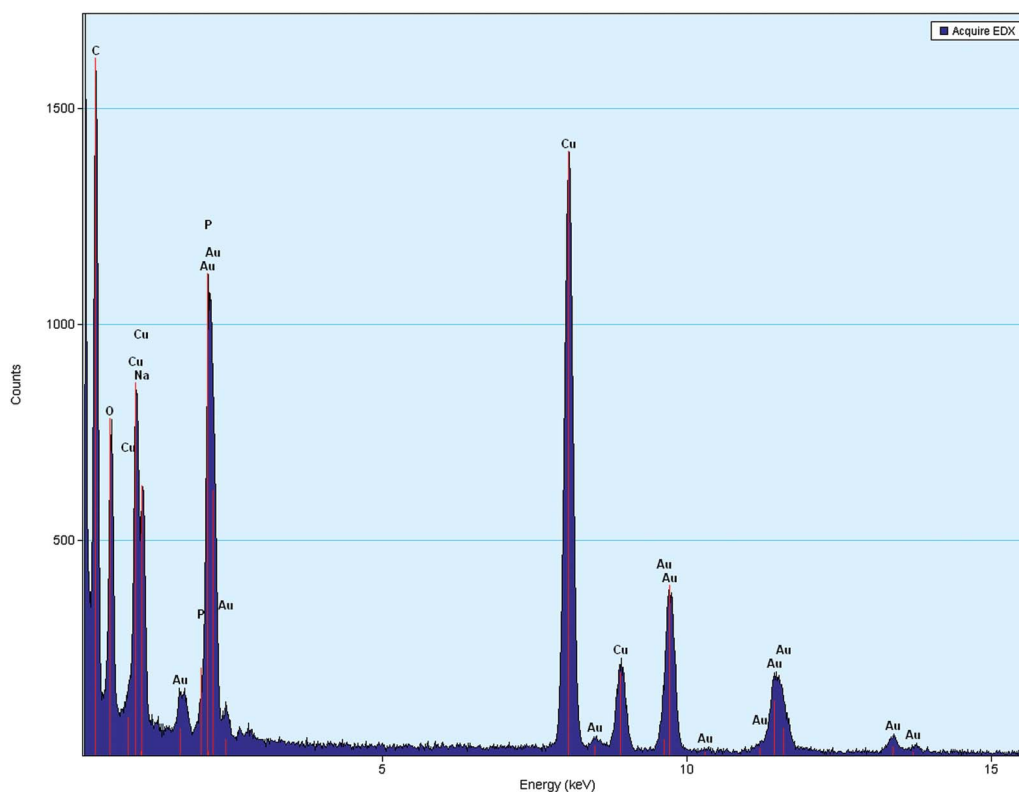


Fig. 3 EDS spectrum of the as-prepared $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs.

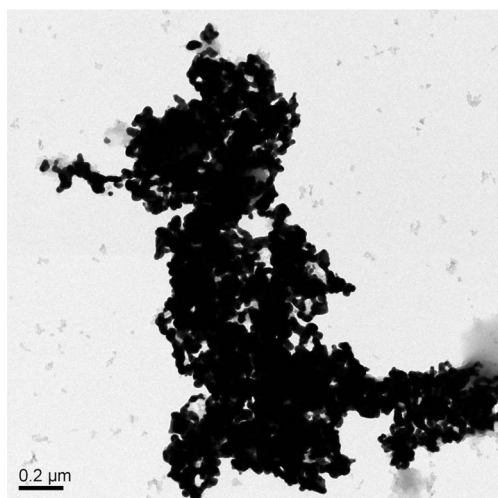


Fig. 4 A typical TEM image of $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs in the presence of Cr^{3+} ions (10 μM).

immediately before use by carefully adding one volume of conc. HNO_3 to three volume of conc. HCl in a glass container (**it is very corrosive!**). Wear chemical splash goggles and thick gloves when using the aqua regia solution in a fumehood. The spent solution is neutralized with sodium bicarbonate and disposed *via* the drain, followed by flushing with copious amounts of water) and then rinsed with Milli-Q water. Briefly, 20 mL of 5 mM HAuCl_4 was added rapidly to the solution of $\text{Na}_5\text{P}_3\text{O}_{10}$ (1 mM, 100 mL), and then sodium borohydride (0.1 M, 5 mL) was slowly added

into the mixed solutions and stirred for 30 min. The color of the gold nanoparticle solution turned a vivid wine-red. Finally, the prepared solution was stored at room temperature for future use and kept there for three months at least. As shown in Fig. 1, these $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs with an average size of 11.13 nm have good dispersion properties.

Colorimetric detection of Cr^{3+} ions

For the detection of Cr^{3+} by using the tripolyphosphate modified gold nanoparticles, different concentrations of Cr^{3+} aqueous solutions were added separately into a 2.0 mL of solution containing $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs, and adjusted the pH value of the mixed solutions to 3.25. Then the mixtures were maintained at room temperature for several minutes, and then the color changed from red to gray-blue.

Results and discussion

Sensing strategy

Scheme 1 outlined a possible sensing mechanism of $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs selectively binding Cr^{3+} . The strong peaks at 889.73 cm^{-1} , 1159.33 cm^{-1} and 1211.29 cm^{-1} were assigned to P–O stretches in $\text{Na}_5\text{P}_3\text{O}_{10}$ ²⁴ and the $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs were also characterized by IR spectroscopy as shown in Fig. 2. However, the $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs had only one weak peak at 1122.3 cm^{-1} . The energy dispersive X-ray spectra (EDS) result (Fig. 3) confirms that the peaks of P and O were attributed to the $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs after complete centrifugation. These are evidences for the existence of $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs. It was shown that $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs were

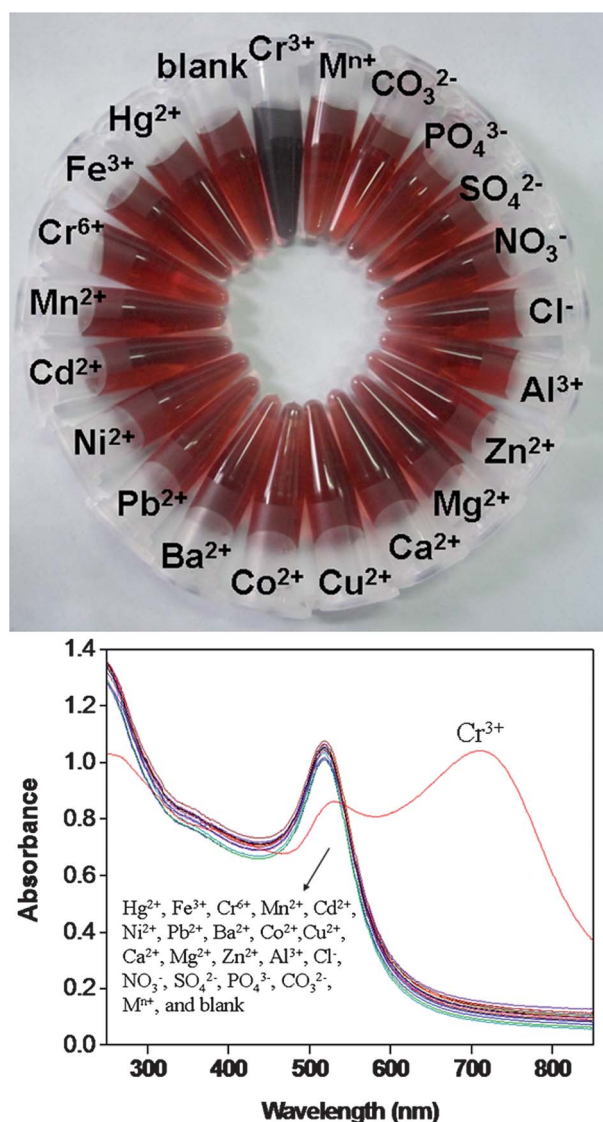


Fig. 5 (Top) Photographic images of $P_3O_{10}^{5-}$ -AuNPs in the presence of various types of ions. (Bottom) UV-vis spectra of $P_3O_{10}^{5-}$ -AuNPs in the presence of different ions (50 μ M). Mn^{n+} contains all of the above interfering ions (50 μ M) with the exception of Cr^{3+} . pH = 3.25.

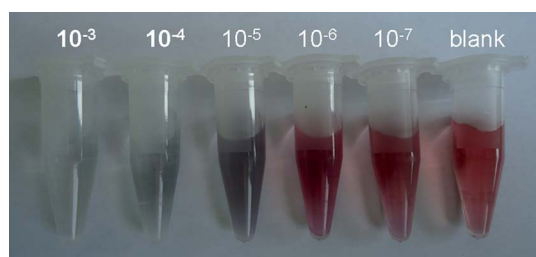


Fig. 6 Various colors of different concentrations of Cr^{3+} were added to the $P_3O_{10}^{5-}$ -AuNPs aqueous solutions.

aggregated in the presence of Cr^{3+} shown in Fig. 4. Therefore, the $Na_5P_3O_{10}$ was absorbed on the surfaces of the AuNPs and the $P_3O_{10}^{5-}$ -AuNPs were aggregated in the presence of Cr^{3+} due to binding with a chelating ligand. It could be explained that

coordination compounds were formed by Cr^{3+} with $P_3O_{10}^{5-}$. Therefore, this approach could be a rapid and sensitive assay method for the detection of Cr^{3+} .

Effects of $Na_5P_3O_{10}$ and pH

In this report, further experiments revealed that many factors such as the concentration of $Na_5P_3O_{10}$ and pH of the aqueous solution, which had influences on the modified gold nanoparticles in the recognition of Cr^{3+} . Although higher concentration of $Na_5P_3O_{10}$ benefited for the homogeneity, dispersibility and size of $P_3O_{10}^{5-}$ -AuNPs and the recognition of Cr^{3+} , however, the $P_3O_{10}^{5-}$ -AuNPs would aggregate together when the concentration of $Na_5P_3O_{10}$ reached 3 mM. Moreover, the concentration of $Na_5P_3O_{10}$ was less responsible for the instability of AuNPs than pH. The $P_3O_{10}^{5-}$ -AuNPs were not stable in one hour when the pH of the aqueous solution was less than 2.50 and the color did not change obviously even the concentration of Cr^{3+} was 10^{-5} M when the pH of the aqueous solution was higher than 4. Above all, it was the reason why the concentration of $Na_5P_3O_{10}$ was 0.8 mM and the pH of the aqueous solution at 3.25 was used in this experiment. Under these optimized conditions, the recognition of Cr^{3+} with $P_3O_{10}^{5-}$ -AuNPs showed a significant color change by this colorimetric assay method.

Selectivity and sensitivity for Cr^{3+}

To investigate the influence of other ions in which $P_3O_{10}^{5-}$ -AuNPs can effectively detect Cr^{3+} , competitive experiments were carried out in the presence of Cr^{3+} (50 μ M) with Hg^{2+} , Fe^{3+} , Cr^{6+} , Mn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Ba^{2+} , Co^{2+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Na^+ , Cl^- , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , NO_3^- and M^{n+} at 50 μ M. Fig. 5 shows that the photographic images and UV-vis spectra of $P_3O_{10}^{5-}$ -AuNPs when various types of ions were added to $P_3O_{10}^{5-}$ -AuNPs aqueous solutions within 1 min, it was clearly shown that only when the sample was added did Cr^{3+} ions induced a distinct color change from red to violet (Fig. 5, top image). The SPR absorption of $P_3O_{10}^{5-}$ -AuNPs was measured with a UV-vis spectrophotometer and its maximum absorption was located at 520 nm. Moreover, Cr^{3+} was also the only ion which resulted in an absorption peak red shift from 520 nm to 725 nm (Fig. 5, bottom image). This red shift was also observed as a color change from red to violet. These results could be evidence for the aggregation of $P_3O_{10}^{5-}$ -AuNPs triggered by Cr^{3+} , which agrees with the TEM images shown in Fig. 4. Effectively, Cr^{3+} triggered the aggregation of $P_3O_{10}^{5-}$ -AuNPs as Cr^{3+} functioned as a bridge among these modified nanoparticles. Other ions did not influence the absorption spectra and indicating that other ions do not interfere in the binding of $P_3O_{10}^{5-}$ -AuNPs with Cr^{3+} . The extremely high selectivity toward Cr^{3+} was attributed to the small K_{sp} (the solubility product constant), and it had a solubility product constant with $CrPO_4$ ($K_{sp} = 2.4 \times 10^{-23}$) over several orders of magnitude more than the other ions. Most importantly, this finding could be a basis for the detection of Cr^{3+} with $P_3O_{10}^{5-}$ -AuNPs as even if all of the above interfering ions were added that did not influence the detection of Cr^{3+} . It was suggested that this method could be suitable for various environmental samples.

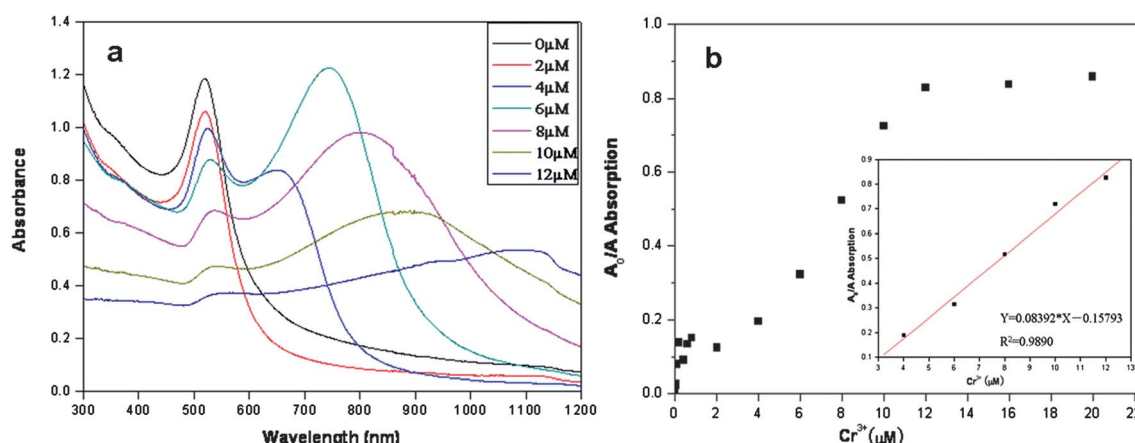


Fig. 7 (a) Surface plasmon resonance absorption change of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs in the presence of different concentrations of Cr^{3+} . (b) The calibration curve for the detection of Cr^{3+} by $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs. The ratio (A_0/A) was plotted against different concentrations of Cr^{3+} . Where A_0 is the UV-vis absorption of the $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs and A is the UV-vis absorption of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs in the presence of different concentrations of Cr^{3+} at 520 nm.

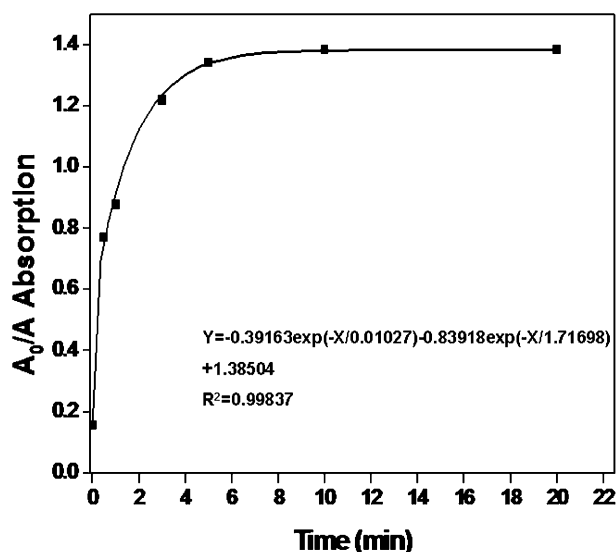


Fig. 8 The aggregation time of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs in the presence of Cr^{3+} (2 μM). It shows that the detection time was rapid within 5 min.

Fig. 6 shows the various colors of the $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs aqueous solutions after the addition of different concentrations of Cr^{3+} . The $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs were utilized for the colorimetric assay of Cr^{3+} under these optimized conditions. As the incorporating concentration of Cr^{3+} increased from 10^{-7} M to 10^{-3} M, the color of these aqueous solutions gradually changed from deep red to gray-blue. As shown in Fig. 4, the color change could be clearly observed when the concentration of Cr^{3+} was higher than 1.0×10^{-7} M, in other words, the detection limit of Cr^{3+} was 1.0×10^{-7} M or so according to this approach of colorimetric assay by naked eye.

According to the above optimized conditions, the minimum detectable concentration of Cr^{3+} was investigated by the color change. Also, UV-vis spectroscopy allowed the detection of low concentrations of Cr^{3+} for the quantitative assay. As shown in Fig. 7, a wide range of Cr^{3+} concentrations from 0.02 μM to 22 μM could be successfully detected in the experiments using

UV-vis spectra. Moreover, the surface plasmon resonance absorption of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs in the presence of different concentrations of Cr^{3+} had two distinct peaks (Fig. 7a), the left absorption peaks had formed due to the dispersion of the modified AuNPs, and the absorption peaks on the right were triggered by the aggregation of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs. Above all, a good linear relationship ($R = 0.9945$) in the range of the concentration of Cr^{3+} from 3 μM to 12 μM was obtained by A_0/A from the left absorption peaks at 520 nm shown in Fig. 7b. Moreover, the limit of quantitative detection (3σ) for Cr^{3+} was found to be 1.2 μM . Furthermore, the colors change of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs in the presence of 2 μM Cr^{3+} within 5 min is shown in Fig. 8.

Application of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs for the analysis of real water samples

To confirm the practical application of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs, the Cr^{3+} concentration of real environmental water samples (Ningbo Environment Monitoring Center, Ningbo, China) was determined by applying this assay method. Firstly, 100 mL water sample was treated with a certain amount of $\text{Na}_2\text{S}_2\text{O}_3$ to convert Cr^{6+} to Cr^{3+} and stirred for 30 min at room temperature. Then the pH of the treated water sample was adjusted to 3.25 with HCl before use. A calibration curve of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs SPR shifted in the presence of different concentrations of Cr^{3+} was prepared (see Fig. 7). The concentration of Cr^{3+} of the real water sample (Ningbo Environment Monitoring Center, Ningbo, China) was from 8.10 μM to 8.20 μM based on the detection results, which was generally in good agreement with the detection result of Cr^{3+} (8.15 μM) by the ICP-AES-based method. Thus, the result demonstrates that the designed colorimetric method is applicable for Cr^{3+} rapid detection in the real water samples.

Conclusions

A highly sensitive, selective and stable colorimetric sensor for the detection of Cr^{3+} has been developed based on the aggregation of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs induced by Cr^{3+} . Cr^{3+} was the only ion which induced the aggregation of $\text{P}_3\text{O}_{10}^{5-}$ –AuNPs which brought

a color change of the sample solution from pink to gray-blue and enhanced the absorption of the SPR of gold nanoparticles. The optimal pH value using $\text{P}_3\text{O}_{10}^{5-}$ -AuNPs was determined to be 3.25. A test of the Cr^{3+} concentration in real environmental samples was done and the results are consistent with the ICP-AES-based method. In principle, this method could provide a promising sensor for on-line detection of Cr^{3+} in real water samples later.

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