

 Open access • Journal Article • DOI:10.1016/J.COLSURFA.2015.02.033

Red-to-blue colorimetric detection of chromium via Cr (III)-citrate chelating based on Tween 20-stabilized gold nanoparticles — [Source link](#)

[Xiaokun Wang](#), [Xiaokun Wang](#), [Yingqin Wei](#), [Shasha Wang](#) ...+2 more authors

Institutions: [Chinese Academy of Sciences](#), [Qufu Normal University](#), [Qilu University of Technology](#)

Published on: 05 May 2015 - [Colloids and Surfaces A: Physicochemical and Engineering Aspects](#) (Elsevier)

Topics: [Ascorbic acid](#)

Related papers:

- [Colorimetric speciation of Cr\(III\) and Cr\(VI\) with a gold nanoparticle probe](#)
- [Non-aggregation based label free colorimetric sensor for the detection of Cr \(VI\) based on selective etching of gold nanorods](#)
- [Detection of the nanomolar level of total Cr\[\(iii\) and \(vi\)\] by functionalized gold nanoparticles and a smartphone with the assistance of theoretical calculation models.](#)
- [Selective colorimetric detection of Cr\(iii\) and Cr\(vi\) using gallic acid capped gold nanoparticles.](#)
- [A rapid colorimetric detection method of trace Cr\(VI\)based on the redox etching of Agcore–Aushell nanoparticles at room temperature](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/red-to-blue-colorimetric-detection-of-chromium-via-cr-iii-4v490iswbx>

See discussions, stats, and author profiles for this publication at: <http://www.researchgate.net/publication/273145180>

Red-to-blue colorimetric detection of chromium via Cr (III)-citrate chelating based on Tween 20-stabilized gold nanoparticles

ARTICLE *in* COLLOIDS AND SURFACES A PHYSICOCHEMICAL AND ENGINEERING ASPECTS · FEBRUARY 2015

Impact Factor: 2.35 · DOI: 10.1016/j.colsurfa.2015.02.033

CITATION

1

DOWNLOADS

40

VIEWS

59

4 AUTHORS, INCLUDING:



[Xiaokun Wang](#)

Hanyang University

6 PUBLICATIONS 30 CITATIONS

SEE PROFILE



[Shasha Wang](#)

Chinese Academy of Sciences

8 PUBLICATIONS 27 CITATIONS

SEE PROFILE



[Lingxin Chen](#)

Chinese Academy of Sciences

198 PUBLICATIONS 2,936 CITATIONS

SEE PROFILE



Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Red-to-blue colorimetric detection of chromium via Cr (III)-citrate chelating based on Tween 20-stabilized gold nanoparticles

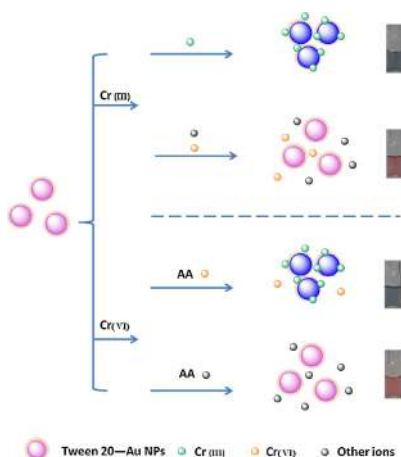
Xiaokun Wang^{a,c}, Yingqin Wei^b, Shasha Wang^a, Lingxin Chen^{a,c,*}^a Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Shandong Provincial Key Laboratory of Coastal Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China^b School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, China^c College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

HIGHLIGHTS

- A simple sensitive colorimetric sensing platform for Cr (III) and Cr (VI) detection.
- The strategy relied on Cr (III)-citrate chelation inducing aggregation of Au NPs.
- Cr (VI) ion was reduced to Cr (III) by ascorbic acid.
- The strategy provided potential for heavy metal speciation analysis.

GRAPHICAL ABSTRACT

A facile and sensitive colorimetric strategy for the determination of Cr (III) and Cr (VI) based on an assembly of Tween 20–Au NPs.



ARTICLE INFO

Article history:

Received 13 December 2014

Received in revised form 13 February 2015

Accepted 20 February 2015

Available online 27 February 2015

Keywords:

Colorimetric detection

Cr (III)

Cr (VI)

Gold nanoparticles

Chelating

Aggregation

ABSTRACT

In this work, a simple “red-to-blue” colorimetric method for highly sensitive and selective determination of Cr (III) and Cr (VI) was presented, which was based on the aggregation of Tween 20-stabilized gold nanoparticles (Tween 20–Au NPs). This strategy relied upon the distance-dependent optical properties of gold nanoparticles (Au NPs), strong chelating between Cr (III) and citrate, and the reduction of Cr (VI) to Cr (III) by ascorbic acid (AA). Cr (III) could chelate with citrate to form a stable Cr (III)-citrate complex and thereby induce the aggregation of Tween 20–Au NPs. Thus, the sensing of Cr (III) and Cr (VI) based on aggregation of Au NPs was developed with the color of the Au NPs changing from red to blue, which was readily seen by the naked eye. The color change and surface plasmon resonance (SPR) absorption were used to monitor Cr (III) and Cr (VI) levels. Under the optimal assay conditions, good linear relationship was obtained, and the detection limit of Cr (III) and Cr (VI) were 0.016 μM and 0.009 μM in standard aqueous solution, respectively. Furthermore, the colorimetric method exhibited a good selectivity over other metal ions and was successfully applied to detect Cr (III) and Cr (VI) in real water samples.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author at: Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Shandong Provincial Key Laboratory of Coastal Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China. Tel.: +86 535 2109130; fax: +86 535 2109130.

E-mail address: lxchen@yic.ac.cn (L. Chen).

<http://dx.doi.org/10.1016/j.colsurfa.2015.02.033>

0927-7757/© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Monitoring of toxic metal ions in aquatic ecosystems is still an important issue due to the adverse impacts on human health and ecological environment via the food chain [1]. Chromium (Cr) pollution originating mainly from waste combustion, electroplating, volcanic, and steel manufacturing [2], commonly exists in two stable oxidation states in aqueous solutions, namely Cr (III) and Cr (VI). Cr (III), as an essential trace element in mammals, is crucial for the metabolism of carbohydrates, proteins, nucleic acids and fats by activating certain enzymes and stabilization of proteins and nucleic acids [3]. However, under overloading conditions, it exhibits high toxicity and can bind DNA, affecting cellular structures and components [4]. Cr (VI) is a well-known carcinogen with negative impact on human skin, lung, stomachs, kidneys and liver, approximately 100–1000 times' toxicity than Cr (III) [5,6]. The U.S. Environmental Protection Agency (EPA), European Community (EC) and World Health Organization (WHO) have recommended that the limits of Cr in drinking water are 100 $\mu\text{g/L}$ (EPA 822-R-06-013), 50 $\mu\text{g/L}$ (98/83/EC) and 50 $\mu\text{g/L}$ (WHO ISBN: 9241546743), respectively.

Increasing concerns over monitoring Cr pollution in aqueous solution have motivated the development of various assays with high sensitivity and selectivity. Current methods of detecting Cr (III) and Cr (VI) include electro-thermal atomic absorption spectroscopy (ETAAS) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], fluorescence resonance energy transfer (FRET) [9], atomic absorption spectrometry (AAS) [10], resonance Rayleigh scattering enhance (RRS) [11], and so on. Although these existing methods can provide excellent sensitivity and selectivity analysis, it is still urgently necessary to explore simpler and more convenient approaches for field assays. Recently, various noble metal nanoparticles have been widely used as attractive colorimetric or surface-enhanced Raman scattering reporters because of their strong surface plasmon resonance (SPR) absorption properties, high extinction coefficient in the visible region and color-tunable behavior that depends on size, shape, and interparticle distance [12–14]. Especially, gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs), have been particularly concerned in detection of metal ions (e.g. Cu^{2+} , Hg^{2+} , Cr^{3+} , Cr^{6+} and Pb^{2+}) and biomolecules because of various advantages such as without requiring sophisticated materials and complex instruments, reading out with the naked eyes, and high stability [15–19]. Typically, Wu's group had developed selective detection of trace Cr (III) in aqueous solution by using 5,5'-dithiobis (2-nitrobenzoic acid)-modified Au NPs, and the detection limit of this method in standard aqueous solution was 1.8 μM [20]. Tseng's group had provided colorimetric method for the detection of Ag^+ and Hg^{2+} based on an assembly of Tween 20-Au NPs [21]. Our group has also designed these kinds of convenient methods for detection various targets, such as surface-enhanced Raman scattering sensing of heparin based on anti-aggregation of functionalized Ag NPs [22], and so on.

So, herein, a convenient and sensitive "red-to-blue" colorimetric sensor for the determination of Cr (III) and Cr (VI) in standard aqueous solutions and tap water samples was presented; this assay relied upon the aggregation of Tween 20-Au NPs at room temperature. Purified citrate-capped Au NPs that stabilized by trace Tween 20 and citrate ions were dispersed in phosphate buffer solution. In the presence of Cr (III), the formation of Cr (III)-citrate chelation led to the aggregation of Tween 20-Au NPs along with obvious change in color and SPR absorption. Cr (VI) can be reduced to Cr (III) by ascorbic acid (AA) [23], and thus, in the simultaneous presence of Cr (VI) and AA, the generated Cr (III) would cause the aggregation of Tween 20-Au NPs. Here, a colorimetric method was developed for Cr (III) and Cr (VI) with satisfactory sensitivity and selectivity. Compared with previous methods (Table S1, Supporting Information), our developed method was maneuverable with good performances,

and all the materials used were inexpensive and available commercially, also the method had been well applied for monitoring Cr (III) and Cr (VI) in real water samples.

2. Experimental

2.1. Material and methods

Hydrogen tetrachloroaurate (III) dehydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), Tween 20 and the used metal salts were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (Beijing, China). Sodium citrate, ascorbic acid (AA), chromic chloride and potassium dichromate were purchased from Aladdin. Other reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (18.2 $\text{M}\Omega \text{cm}$ specific resistance) purified by a Cascada TM LS Ultrapure water system (Pall Corp., USA).

2.2. Apparatus

UV-vis absorption spectra were recorded on a Thermo Scientific NanoDrop 2000 C spectrophotometer (Gene Company Ltd., USA). Transmission electron microscopy (TEM) analysis was performed on a JEM-1230 electron microscope (JEOL, Ltd., Japan) operating at 100 kV. Zeta potential measurements were performed on Malvern Zetasizer Nano-ZS90 (ZEN3590, Malvern Instruments Ltd., U.K.). All glasswares used in the experiments were soaked with freshly prepared aqua regia, and then extensively washed in deionized water and dried in air.

2.3. Synthesis of Tween 20-Au NPs

Au NPs were prepared with the sodium citrate reduction method according to the published literatures with necessary modification [24,25]. In brief, 100 mL of 1.0 mM HAuCl_4 was heated to reflux with vigorous stirring in a round-bottom flask fitted with a reflux condenser, and then 10 mL of 38.8 mM sodium citrate was rapidly added. The mixture was kept boiling for another 20 min, during which its color changed from pale yellow to wine red. Finally, the solution was cooled to room temperature with continuous stirring. The size of the citrate-capped Au NPs determined by TEM image was about 13 nm. Herein, for Au NPs, citrate acted as both a reductant for synthesis and a surface passivant for stabilization [26–28]. The prepared Au NPs were first centrifuged at 12,000 rpm for 12 min to remove the free citrate ions in the solution and then dispersed in Millipore-Q water containing trace Tween 20. Tween 20 was added in order to stabilize the centrifuged citrate-Au NPs against the high salt conditions. So, Tween 20-Au NPs were synthesized.

2.4. Detection of Cr (III) and Cr (VI) using Tween 20-Au NPs

The experiments were performed at room temperature, and pH 6.4 was selected as the optimal testing pH value. For Cr (III) sensing, 10 μL of Cr (III) solution was added to 990 μL phosphate buffer solutions (PBS) containing 200 μL Tween 20-Au NPs. For Cr (VI) sensing, 10 μL of Cr (VI) solution was added to 990 μL of PBS containing 200 μL of Tween 20-Au NPs and 10 μM AA. After equilibrating for the optimal incubation time, UV-vis absorption spectra were recorded. Sensitivity of this method toward Cr (III) and Cr (VI) was evaluated in the similar way, as above 2.4. In the presence of different concentrations of Cr (III) solutions (from 0 to 10 μM) and Cr (VI) solution (from 0 to 3.5 μM), respectively, equilibrating for the optimal incubation time, UV-vis absorption spectra were recorded.

2.5. Selectivity study

In the experiments of selectivity procedure, all samples were prepared in the similar way, under the same optimized conditions. We investigated the selectivity of our method for Cr (III) and Cr (VI) over other metal ions including Na^+ , Hg^{2+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Li^+ , Cd^{2+} , Ca^{2+} , Pb^{2+} , Fe^{3+} and Fe^{2+} .

2.6. Analysis of real water samples

Tap water samples were collected from our laboratory after flowing for about 5 min. River water samples were collected from Dagujiahe River (Yantai, China). They were collected into Teflon bottle and filtered through a $0.2\ \mu\text{m}$ membrane. The water samples were directly analyzed or stored at 4°C for use. Before the spiking procedure, the samples were analyzed by ICP-MS and were found to be free of Cr contamination. And then, $100\ \mu\text{L}$ of the real water samples were spiked with standard Cr (III) and Cr (VI) solutions, respectively. The spiked samples were subsequently diluted to $1000\ \mu\text{L}$ by PBS containing Tween 20-Au NPs, Tween 20-Au NPs and AA, respectively.

2.7. Safety consideration

Aqua regia has strong oxidizing capacity and adverse effects on human health; thus, all of the experiments involving aqua regia should be performed with gloves and protective glasses. Most of tested metal ions are highly toxic and have adverse effects on human health; thus, the waste solutions of the experiments should be collectively reclaimed to avoid polluting the environment.

3. Results and discussion

3.1. Sensing principle

Fig. 1 presents the sensing principle of the colorimetric method for the detection of Cr (III) and Cr (VI) based on aggregation of Tween 20-Au NPs. In this colorimetric approach, we took advantage of the fact that, one Cr (III) could bind two citrates which were attached to the Au NPs, and thus would induce the aggregation of Tween 20-Au NPs [29]. On the other hand, Cr (VI) was not able to trigger the aggregation of Tween 20-Au NPs, which was probably due to the strong electrostatic repulsion between negatively charged Cr (VI) and Tween 20-Au NPs. That is, Tween 20-Au NPs were still stable by comparing with the zeta potentials of Tween 20-Au NPs ($-28.7\ \text{mV}$) and Cr (VI)-Tween 20-Au NPs ($-28.5\ \text{mV}$). Interestingly, AA is highly efficient in the reduction of Cr (VI) to Cr (III) [30]. AA-treated Cr (VI) could also induce the aggregation of Tween 20-Au NPs, and thereby Cr (VI) could also be detected.

In this method, Au NPs were prepared using the sodium citrate reduction method according to the reported methods [24,25] with necessary modification. Based on the previous work and the present experimental observations [24–28], it could be concluded that on one hand citrate acted as a reductant for Au NPs synthesis, and on the other hand the remained citrate played as a passivant for Au NPs surface stabilization. Hence, the prepared Au NPs were first centrifuged at $12,000\ \text{rpm}$ for 12 min to remove the free citrate ions in the solution and then dispersed in Millipore-Q water containing trace Tween 20. Tween 20 was added in order to stabilize the centrifuged citrate-Au NPs against the high salt conditions. In the presence of Cr (III), it could chelate the adsorbed citrate on the surface of Au NPs [29], and thereby induce the aggregation of Tween 20-Au NPs followed by an obvious color change from red to blue. In addition, in the coexistence of Cr (VI) and AA, Cr (VI) could be reduced to Cr (III), resulting in the aggregation of Tween 20-Au

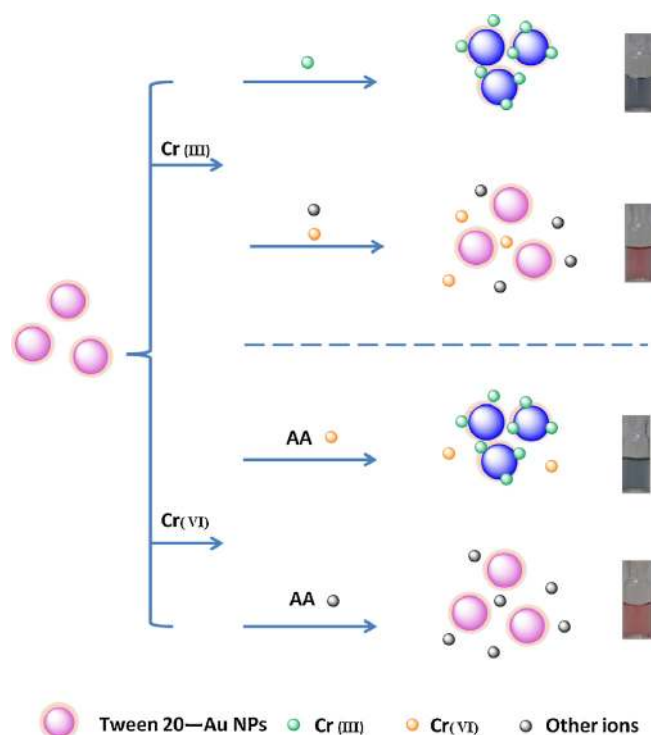


Fig. 1. Schematic illustration of the proposed method for measuring Cr (III) and Cr (VI) via Cr (III)-citrate chelating based on the Tween 20-Au NPs.

NPs accompanied with obvious change in color and SPR absorbance. Therefore, Cr (III) and Cr (VI) could be sensed optically by this way.

To demonstrate the feasibility of our colorimetric sensor strategy for Cr (III) and Cr (VI) detection, UV–vis absorption spectra, TEM images and photographs were utilized to characterize the assay. As shown in Fig. 2A (a and b), the absorbance of Tween 20-Au NPs without and with AA appeared at $520\ \text{nm}$ and the solutions were still red (photographs a and b), which indicated Tween 20-Au NPs were well dispersed in $10\ \text{mM}$ PBS. Fig. 2A (c) indicated that without AA, Cr (VI) could not lead to Tween 20-Au NPs aggregation. However, as clearly shown in Fig. 2A (d and e), in the presence of $2.0\ \mu\text{M}$ Cr (III) or in the simultaneous presence of $2.0\ \mu\text{M}$ Cr (VI) and $10\ \mu\text{M}$ AA, color change (photographs d and e) and the aggregation of Tween 20-Au NPs occurred. Moreover, dispersion and aggregation of Tween 20-Au NPs were also characterized, respectively as shown in Fig. 1B. So, all the results confirmed the colorimetric assay was feasible for the detection of Cr (III) and Cr (VI).

3.2. Optimization of sensing conditions

In order to obtain better performance of the proposed method, several related conditions were evaluated including pH, concentration of AA and incubation time. The absorbance values of sensing solution at $520\ \text{nm}$ and $660\ \text{nm}$ were employed to represent the relative amounts of dispersed and aggregated Tween 20-Au NPs, respectively.

The effect of pH on the aggregation of Tween 20-Au NPs in PBS were investigated, in the presence of $3.5\ \mu\text{M}$ Cr (III) and in the simultaneous presence of $2.5\ \mu\text{M}$ Cr (VI) and $10\ \mu\text{M}$ AA. Fig. S1A (Supporting Information) shows the effect of pH in the range from 6.0 to 8.5. The ratio of A_{660}/A_{520} was reduced with the increase of pH value because alkaline solution conditions could destroy chelating reaction between Cr (III) and citrate ions. As shown in Fig. S1B (Supporting Information), pH at 6.4 was also suitable for the detection

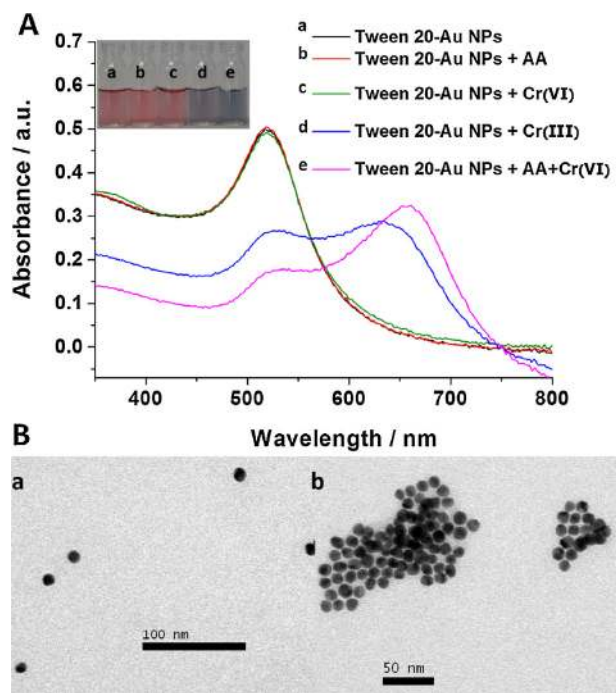


Fig. 2. (A) UV-vis absorption spectra (inset photographs is colorimetric response) of (a) Tween 20-Au NPs; (b) Tween 20-Au NPs + 10 μM AA; (c) Tween 20-Au NPs + 2.0 μM Cr (VI); (d) Tween 20-Au NPs + 2.0 μM Cr (III); (e) Tween 20-Au NPs + 10 μM AA + 2.0 μM Cr (VI); (B) TEM images of (a) dispersed and (b) aggregated Tween 20-Au NPs.

of Cr (VI). As a result, pH value at 6.4 (10 mM PBS) was employed in the following experiments.

The concentration of AA played a crucial role in Cr (VI) sensing system. As shown in Fig. S2 (Supporting Information), when the concentration of AA was 10 μM , the ratio of A_{660}/A_{520} reached the equilibrium stage, thus, we used 10 μM AA in this experiment. As shown in Fig. S3 (Supporting Information), incubation time was also investigated with the addition of different concentrations of Cr (III) and Cr (VI), respectively. As shown in Fig. S3A (Supporting Information), the ratio of A_{660}/A_{520} became constant at different concentrations of Cr (III) after 25 min, and as shown in Fig. S3B (Supporting Information), the optimum incubation time was also about 20–25 min for the detection of Cr (VI). Finally, we chose 25 min as the incubation time to carry out the experiment.

3.3. Sensitivity and selectivity of the sensor

Under optimal sensing conditions, sensitivity of our approach toward Cr (III) and Cr (VI) was evaluated. As shown in Fig. 3A, with the increase of the concentration of Cr (III), the absorption peak at 520 nm decreased while peak at 660 nm increased, accompanied with obvious color change (inset of Fig. 3A). Fig. 3B shows the ratio of A_{660}/A_{520} tended to be constant over the concentration of 5.0 μM , and a good linear relationship, $y = -0.153 + 0.639x$, was obtained over the range of 0.05–5.0 μM (inset of Fig. 3B) with the correlation coefficient of 0.989.

For Cr (VI) sensing system, as shown in Fig. 4A, obvious changes in the absorption peak and color occurred. Fig. 4B showed a satisfying linear relationship $y = -0.101 + 0.987x$ over the range of 0.02–2.5 μM with the correlation coefficient of 0.987. The detection limit of Cr (III) and Cr (VI) was 0.016 μM and 0.009 μM , respectively, calculated by $3\sigma/S$ (S meant the slope of the linear equation; σ meant the standard deviation of six blank measurements). Thus, the detection limit of Cr (III) was obtained,

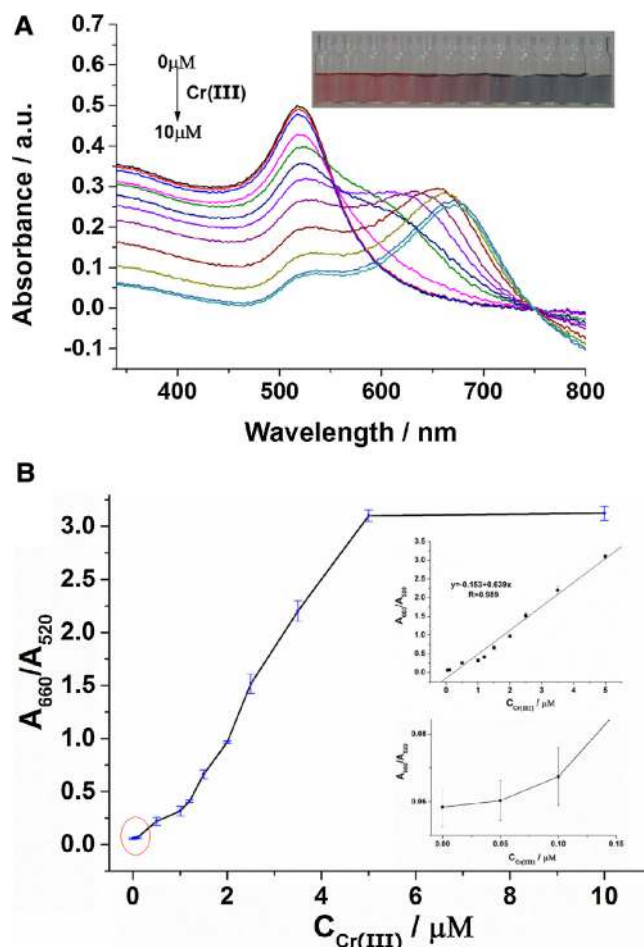


Fig. 3. (A) UV-vis absorption spectra changes of the proposed probe with the addition of different concentrations of Cr (III) (from 0 μM to 10 μM) and (B) Plots of A_{660}/A_{520} versus the concentration of Cr (III) ($r = 0.989$). Inset photograph is colorimetric response. The error bars represent the standard deviations based on three independent measurements.

$DL = 3 \times (0.003343/0.639) = 0.016 \mu\text{M}$, and the detection limit of Cr (VI) was obtained, $DL = 3 \times (0.003092/0.987) = 0.009 \mu\text{M}$, which confirmed the sensor had excellent sensitivity.

To realize the selectivity of the “red-to-blue” colorimetric method toward Cr (III) and Cr (VI), other metal ions were tested by the sensing strategy under the same optimal conditions. As shown in Fig. 5A, compared with 1.0 μM Cr (III), 100 μM Na^+ , Hg^{2+} , Al^{3+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Li^+ , Cd^{2+} , Ca^{2+} , Cr (VI), Fe^{3+} and Fe^{2+} , and 50 μM Cu^{2+} and Pb^{2+} , could not induced the aggregation of Tween 20-Au NPs. And Fig. 5B showed that 100 μM of Na^+ , Hg^{2+} , Al^{3+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Li^+ , Ca^{2+} , Fe^{3+} and Fe^{2+} , 50 μM of Cu^{2+} and Pb^{2+} , and 25 μM of Cd^{2+} , could not affected the detection of 1.0 μM Cr (VI). In addition, as we know, Hg^{2+} could be reduced to Hg (0) and formed Hg-Au alloys [31,32], which may disturb the surface of Au NPs. However, in this sensing method, 100 μM of Hg^{2+} could not interfere with the detection process. It is mainly due to the concentration of AA and reaction condition, as shown in Fig. S4 (Supporting Information). In the presence of 10 μM AA, Tween 20-Au NPs was still stable, without any color change. In the presence of 100 μM AA, obvious change in color and SPR absorption were obtained. Considering 10 μM AA had been selected as the optimal concentration in this sensing system, it could be concluded that even the high concentration of Hg^{2+} (100 μM) had no interference on Cr (VI) detection. Therefore, all of the results indicated that our colorimetric method exhibited a satisfying selectivity for Cr (III) and Cr (VI).

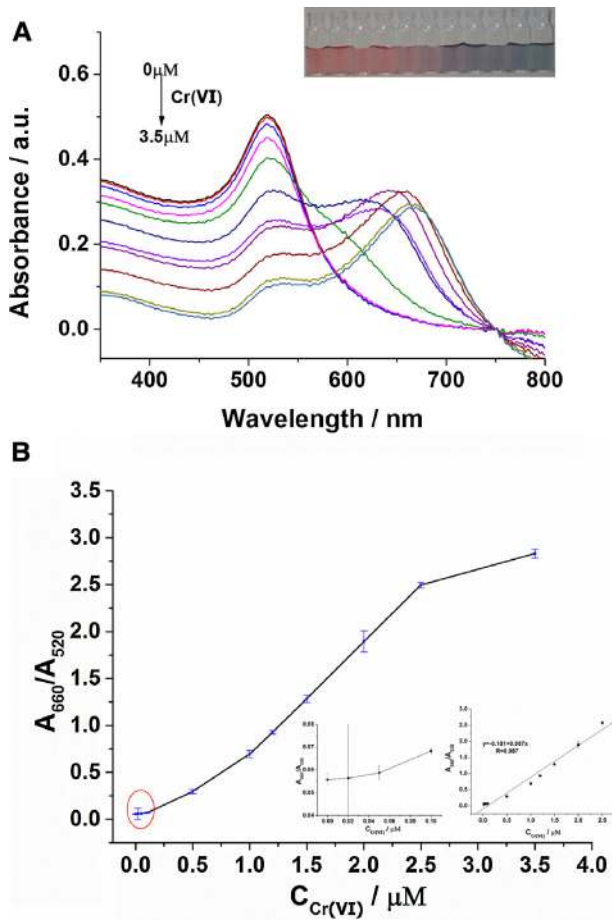


Fig. 4. (A) UV-vis absorption spectra of the proposed probe with the addition of different concentrations of Cr (VI) (from 0 μM to 3.5 μM) and (B) Plots of A_{660}/A_{520} versus the concentration of Cr (VI) ($r=0.987$). Inset photograph is colorimetric response. The error bars represent the standard deviations based on three independent measurements.

3.4. Practical application

To evaluate its practical applications, the method was further tested on real samples of tap water and river water. In contrast to standard aqueous solution, real water sample was complicated environmental fluids, suffering from matrix effect. In order to obtain accurate test results in real water samples, linear relationships were further studied. As shown in Fig. S5A (Supporting Information), the ratio of A_{660}/A_{520} increased linearly with the concentration of Cr (III) in tap water samples, and a good linearity

Table 1

The recovery values of spiked Cr (III) in tap water and river water samples, and the relative standard deviation (RSD) values of each sample obtained by three parallel measurements.

Sample	Spiked (μM)	Detected (μM)	Recovery (%)	RSD (%)
Tap water	0	ND ^a	–	–
	0.05	0.046	92	1.47
	0.50	0.51	100.2	2.09
	1.00	1.06	106	1.12
	1.50	1.37	91.3	0.58
	2.50	2.43	97.2	0.72
River water	0	ND ^a	–	–
	0.20	0.19	95	0.81
	1.00	1.03	103	0.94
	2.00	1.97	98.5	1.43

^a Not detected.

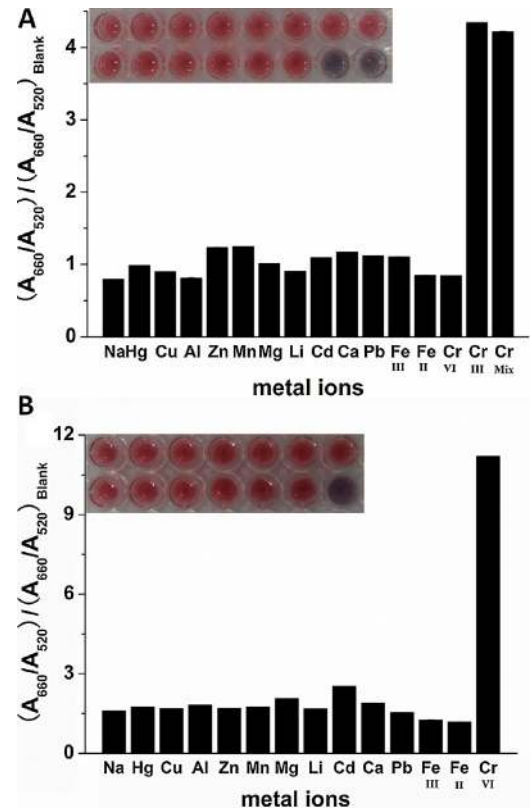


Fig. 5. The value of $(A_{660}/A_{520})/(A_{660}/A_{520})_{\text{Blank}}$ of the proposed sensor (A) in the presence of 1.0 μM Cr (III), 50 μM of Cu^{2+} , Pb^{2+} and 100 μM other metal ions respectively, (B) in the presence of 1.0 μM Cr (VI), 50 μM of Cu^{2+} and Pb^{2+} , 25 μM of Cd^{2+} and 100 μM other metal ions respectively. Inset photograph is colorimetric response.

Table 2

The recovery of spiked Cr (VI) in tap water and river water samples, and the RSD values of each sample obtained by three parallel measurements.

Sample	Spiked (μM)	Detected (μM)	Recovery (%)	RSD (%)
Tap water	0	ND ^a	–	–
	0.05	0.047	94	1.11
	0.50	0.503	100.6	0.303
	1.00	1.12	112	0.59
	1.50	1.47	98	0.76
	2.00	2.03	101.5	1.03
River water	0	ND ^a	–	–
	0.10	0.11	110	0.76
	1.00	1.02	102	1.30
	2.00	1.98	99	0.94

^a Not detected.

$y = -0.0484 + 0.570x$ was obtained. For the detection of Cr (VI) in tap water samples, linear relation was $y = 0.0503 + 0.901x$ shown in Fig. S5B. As shown in Tables 1 and 2, satisfying recoveries were attained. For example, Table 1 lists the recovery values of 91.3–106% with relative standard deviation (RSD) values of 0.72–2.09% for spiked five concentrations of Cr (III) in tap water samples. Recovery values of 99–110% with RSD values of 0.76–1.30% were obtained for spiked three concentrations of Cr (VI) in river water samples, as seen in Table 2. These results clearly demonstrated the developed “red-to-blue” colorimetric method was potentially applicable for the detection of Cr (III) and Cr (VI) in real water samples.

4. Conclusions

A “red-to-blue” colorimetric method based on the aggregation of Tween 20-Au NPs was developed for highly sensitive and

selective detection of Cr (III) and Cr (VI). This convenient assay avoided expensive instruments and complicated design/synthesis processes, and allowed detecting two valence state of Cr by simple UV–vis spectroscopy as well as naked eyes. Moreover, under the optimal sensing conditions, this strategy provided high sensitivity for Cr (III) and Cr (VI) in aqueous solutions (0.016 μM and 0.009 μM , respectively), and it also exhibited satisfactory selectivity over other metal ions. Furthermore, compared with some reported methods listed in Table S1 (Supporting Information), the developed red-to-blue colorimetric detection of chromium via Cr (III)–citrate chelating based on Tween 20-stabilized Au NPs proved to be an ideal candidate sensing strategy, which successfully detect both Cr (III) and Cr (VI) with satisfactory selectivity and sensitivity. What is more, this method provided a great potential application in real water samples. All the results substantially indicated that the developed strategy were potentially feasible for metal ions and their species monitoring/analysis.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant 21275158), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2015.02.033>.

References

- [1] L. Campbell, D.G. Dixon, R.E. Hecky, A review of mercury in lake Victoria, east Africa: implications for human and ecosystem health, *J. Toxicol. Environ. Health. B* 6 (2003) 325–356.
- [2] R.G. Kieber, J.D. Willey, S.D. Zvalaren, Chromium speciation in rainwater: temporal variability and atmospheric deposition, *Environ. Sci. Technol.* 36 (2002) 5321–5327.
- [3] W. Mertz, K. Schwarz, Impaired intravenous glucose tolerance as an early sign of dietary necrotic liver degeneration, *Arch. Biochem. Biophys.* 58 (1955) 504–506.
- [4] A.R. Walsh, J. Ohalloran, A.M. Gower, Some effects of elevated levels of chromium (III) in sediments to the mullet chelon labrosus (R), *Ecotoxicol. Environ. Saf.* 27 (1994) 168–176.
- [5] V. Gómez, M.P. Callao, Chromium determination and speciation since 2000, *TrAC-Trend. Anal. Chem.* 25 (2006) 1006–1015.
- [6] R. Rakhunde, L. Deshpande, H. Juneja, Chemical speciation of chromium in water: a review, *Crit. Rev. Environ. Sci. Technol.* 42 (2012) 776–810.
- [7] S.C. Nielsen, S. Sturup, H. Spliid, E.H. Hansen, Selective flow injection analysis of ultra-trace amounts of Cr (VI), preconcentration of it by solvent extraction, and determination by electrothermal atomic absorption spectrometry (ETAAS), *Talanta* 49 (1999) 1027–1044.
- [8] M.M. Guerrero, E. Alonso, J.M. Pavon, M.T. Cordero, A. Torres, On-line preconcentration using chelating and ion-exchange minicolumns for the speciation of chromium (III) and chromium (VI) and their quantitative determination in natural waters by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 27 (2012) 682–688.
- [9] Z.G. Zhou, M.X. Yu, H. Yang, K.W. Huang, F.Y. Li, T. Yi, C.H. Huang, FRET-based sensor for imaging chromium (III) in living cells, *Chem. Commun.* 29 (2008) 3387–3389.
- [10] C.H. Williams, D.J. David, O. Lismaa, The determination of chromic oxide in faeces samples by atomic absorption spectrophotometry, *J. Agric. Sci.* 59 (1962) 381–385.
- [11] M. Chen, H.H. Cai, F. Yang, D. Lin, P.H. Yang, J. Cai, Highly sensitive detection of chromium (III) ions by resonance Rayleigh scattering enhanced by gold nanoparticles, *Spectrochim. Acta A* 118 (2014) 776–781.
- [12] C. Burda, X. Chen, R. Narayanan, M. El-Sayed, Chemistry and properties of nanocrystals of different shapes, *Chem. Rev.* 105 (2005) 1025–1102.
- [13] R. Aakawa, H. Kawasaki, Functionalized nanoparticles and nanostructured surfaces for surface-assisted laser desorption/ionization mass spectrometry, *Anal. Sci.* 26 (2010) 1229–1240.
- [14] X.K. Wang, L. Chen, L.X. Chen, Colorimetric determination of copper ions based on the catalytic leaching of silver from the shell of silver-coated gold nanorods, *Microchim. Acta* 181 (2014) 105–110.
- [15] W. Ren, C.Z. Zhu, E.K. Wang, Enhanced sensitivity of a direct SRES technique for Hg²⁺ detection based on the investigation of the interaction between silver nanoparticles and mercury ions, *Nanoscale* 4 (2012) 5902–5909.
- [16] Y. Xu, X.M. Yang, S.S. Zhu, Y. Dou, Selectively fluorescent sensing of Cu²⁺ based on lysine-functionalized, *Colloids Surf. A: Physicochem. Eng. Aspects* 450 (2014) 115–120.
- [17] Y.Q. Wang, B. Yan, L.X. Chen, SERS tags: novel optical nanoprobe for bioanalysis, *Chem. Rev.* 113 (2013) 1391–1428.
- [18] P. Rattananat, W. Dungchai, D.M. Cate, W. Siangproh, J. Volckens, O. Chailapakul, C.S. Henry, A microfluidic paper-based analytical device for rapid quantification of particulate chromium, *Anal. Chim. Acta* 800 (2013) 50–55.
- [19] Y.J. Lai, W.L. Tseng, Role of 5-thio-(2-nitrobenzoic acid)-capped gold nanoparticles in the sensing of chromium (VI): remover and sensor, *Analyst* 136 (2011) 2712–2717.
- [20] Y.Q. Dang, H.W. Li, B. Wang, L. Li, Y. Wu, Selective detection of trace Cr³⁺ in aqueous solution by using 5,5'-dithiobis (2-nitrobenzoic acid)-modified gold nanoparticles, *ACS Appl. Mater. Interface* 1 (2009) 1533–1538.
- [21] C.Y. Lin, C.J. Yu, Y.H. Lin, W.L. Tseng, Colorimetric sensing of silver (I) and mercury (II) ions based on an assembly of tween 20-stabilized gold nanoparticles, *Anal. Chem.* 82 (2010) 6830–6837.
- [22] X.K. Wang, L. Chen, X.L. Fu, L.X. Chen, Y.J. Ding, Highly sensitive surface-enhanced Raman scattering sensing of heparin based on antiaggregation of functionalized silver nanoparticles, *ACS Appl. Mater. Interface* 5 (2013) 11059–11065.
- [23] D.M. Stearns, K.E. Wetterhahn, Reaction of chromium (VI) with ascorbate produces chromium (V), chromium (IV), and carbon-cased radicals, *Chem. Res. Toxicol.* 7 (1994) 219–230.
- [24] G. Frens, Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions, *Nature* 241 (1973) 20–22.
- [25] J. Turkevich, P.C. Stevenson, J. Hillier, A study of the nucleation and growth processes in the synthesis of colloidal gold, *Trans. Faraday Soc.* 11 (1951) 55–75.
- [26] M.K. Chow, C.F. Zukoski, Gold sol formation mechanisms: role of colloidal stability, *J. Colloid Interface Sci.* 165 (1994) 97–109.
- [27] S. Biggs, P. Mulvaney, C.F. Zukoski, F. Grieser, Study of anion adsorption at the gold-aqueous solution interface by atomic force microscopy, *J. Am. Chem. Soc.* 116 (1994) 9150–9157.
- [28] J.F. Wall, F. Grieser, H.F. Zukoski, 61801, USA b Advanced Mineral Products Research Centre, School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia, *J. Chem. Soc. Faraday Trans.* 93 (1997) 4017–4020.
- [29] C. Gabriel, C.P. Raptopoulou, A. Terzis, V. Tangoulis, C. Mateescu, A. Salifoglou, pH-specific synthesis and spectroscopic, structural, and magnetic studies of a chromium (III)–citrate species. Aqueous solution speciation of the binary chromium (III)–citrate system, *Inorg. Chem.* 46 (2007) 2998–3009.
- [30] X.R. Xu, H.B. Li, X.Y. Li, J.D. Gu, Reduction of hexavalent chromium by ascorbic acid in aqueous solutions, *Chemosphere* 57 (2004) 609–613.
- [31] Y.C. Shih, C.Y. Ke, C.J. Yu, C.Y. Lu, W.L. Tseng, Combined Tween 20-stabilized gold nanoparticles and reduced graphite oxide–Fe₃O₄ nanoparticle composites for rapid and efficient removal of mercury species from a complex matrix, *ACS Appl. Mater. Interface* 6 (2014) 17437–17445.
- [32] I. Ojea-Jiménez, X. López, J. Arbiol, V. Puntes, Citrate-coated gold nanoparticles as smart scavengers for mercury (II) removal from polluted waters, *ACS Nano* 6 (2012) 2253–2260.