



## Detection of chromium(III) in drinking water with modified gold nanoparticle

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### ABSTRACT

Given that gold nanoparticle has been taken into consideration in the past few years and it has been widely used as a sensor, the synthesis of gold nanoparticle with specific groups on its surface is of great importance. Therefore, the available and straightforward method was synthesis with 1-[1-hydroxy naphthyl]-6-nitro-2-naphthol-4-sulfonate (HNS) as a capping and reduction agent for a gold nanoparticle. The structure of HNS-gold nanoparticle was characterized by surface plasmon resonance (SPR) peak around 525 nm, TEM, TGA, FT-IR spectroscopy, Dynamic light scattering (DLS) and the size of the nanoparticles with transmission electron microscopy (TEM) was observed to 25–35 nm. For sensing of chromium (III) ions, the surface plasmon resonance (SPR) peak shift was used and it is linearly related to the concentration of Cr(III) ions in the 50–500 nM, the LOD was found to be 20 nM.

**Keywords:** Drinking water; Gold nanoparticle; Sensor; Cr<sup>3+</sup> ions

### 1. Introduction

The determination of different metals in the drinking water, which is one of the ways to import these elements to the human body, has been considered as one of the significant issues by scientists in recent years [1]. Because some metal ions are well known for their biological activity in most living systems, and an excessive amount of these metals in the human body can cause various diseases [2–4].

Chromium is one of the metals whose excessive use in industries such as metalworking, colour stability to prevent corrosion of metals, catalyze, the oil industry and the chemical industry in the electroplating is some of the factors that create the pollution of drinking water in the rivers and lakes of the earth. One of the elements that the trace of it is significant and necessary for humans and animals is chromium. It is so because of its application in metabolism by stabilization of nucleic acids and proteins and also making active specific enzymes [5]. However, the structure of cellular in the result of the excess of Cr(III) in the human body can be damaged because of its bind to DNA. Beside the point, insulin resistance is due to the shortage of this metal.

Thereby, the analysis and measurement of Cr(III) ions in biological and environmental samples have become increasingly significant. Spectrofluorometry [5], atomic absorption spectrometry (AAS) [6], and electrochemical methods [7,8] are several methods which are used for detection of Cr<sup>3+</sup> ions. However, in these devices, the sample preparation is costly and difficult; therefore, it is of high importance to find a more accessible and more cost-effective method to detect Cr<sup>3+</sup> ions in an aqueous environment. Synthesis of gold nanoparticle and modification with different organic groups is one of the essential techniques that have a very high potential for the determination of quantitative compounds such as metals in different environments [6,7]. One of the unique features of the gold nanoparticle is their size during the synthesis, modifying the surface of these particles using specific organic groups with straightforward, easy, and environmentally friendly methods. Besides, one unique property of these particles is their optical property by increasing the diameter of particles, the UV-VIS wavelength, and colour of solution change. The sum of these features causes gold nanoparticles to be considered a fast, simple, and cost-effective method [8–13].

As you know well, for determination of toxic compounds with the phenomenon of aggregation in the sur-

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face of the gold nanoparticle, the changing of colour from red to blue and UV-VIS wavelength are used [14,15]. In this research, modified gold nanoparticle was synthesized by eriochrome black T. In addition to the features listed above such as a fast, cost-effective and straightforward, it can be also detection of only chromium in an aqueous environment. This determination is performed both qualitatively and quantitatively. Its qualitative detection is the bare eye detection in a red-to-blue colour change and the quantitative detection using the surface plasma band and change in the UV-VIS wavelength in the presence of chromium (III).

## 2. Experimental

### 2.1. Apparatus, reagents, and materials

The UV-Visible spectroscopy was obtained on a Cary 100 at room temperature with a double beam. For the FT-IR spectroscopy, the FT-IR was measured on a Bruker Vertex 70 spectrophotometer. The transmission electron microscopy (TEM) measurements were performed on an H-7500 transmission electron microscope operated at an accelerating voltage of 80 kV. Malvern ZEN3600 was used for measurement of Dynamic light scattering (DLS). Thermogravimetric analysis (TGA) of Netzsch STA.

For cleaning the glassware, the freshly prepared concentrated hydrochloric acid and concentrated nitric acid with a ratio (HCl: HNO<sub>3</sub>) 3:1 was used, rinsed thoroughly in water, and dried in air. The eriochrome black T, HAuCl<sub>4</sub>, and other chemicals were of analytical reagent grade and were purchased from Aldrich and Merck. Double-distilled water was used for the preparation of all solutions.

### 2.2. Synthesis of gold nanoparticle modified with 1-[1-Hydroxy Naphthyl]-6-nitro-2-naphthol-4-sulfonate (HNS-GNPs)

For controlling diameter and surface plasmon band of a gold nanoparticle, different parameters such as a concentration of the eriochrome black T, temperature and time reaction were measured by UV-visible spectroscopy and bare eye by the maximum peak at 520–525 nm and change colour. Briefly, in optimized condition, 10 ml of 0.0001 M of 1-[1-hydroxy naphthyl]-6-nitro-2-naphthol-4-sulfonate was freshly prepared as a stabilizing and reducing agent was added to 10 ml of 0.001 M of HAuCl<sub>4</sub> solution at 50°C. After 3 h, the solution colour was changed to red which confirms the reduction of Au<sup>3+</sup> to Au<sup>0</sup> [16,17]. The HNS-GNPs was centrifuged and re-dispersed in water. The dispersion and centrifugation process was repeated thrice to remove any unreacted Au<sup>3+</sup> ions or 1-[1-hydroxy naphthyl]-6-nitro-2-naphthol-4-sulfonate from the final product.

### 2.3. Sensing studies of HNS-GNPs

For the colorimetric response of nanosensor, 100 nM of Ca<sup>+</sup>, Ni<sup>+</sup>, Mn<sup>2+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, and Cr<sup>3+</sup> were added into 2.00 mg HNS-GNPs in 4 ml of water and monitored by UV-spectrophotometer at room

temperature. The photographs were taken with a digital camera.

### 2.4. Sensing studies of HNS-GNPs for the detection of Cr<sup>3+</sup> ions

Different concentration of Cr<sup>3+</sup> (25 nM–600 nM) was mixed with 2 mg of dispersed HNS-GNPs in 4 ml water at ambient temperature for 10 min. The absorbance peak was recorded by using UV-vis absorption spectra.

### 2.5. The effect of pH

To monitor the efficiency of the sensor in different pHs, 2 mg of the HNS-GNPs was added to 4 ml of a solution with different pH in the range of 2–10 and record the absorbance ratio ( $A_{655}/A_{525}$ ) with the spectrophotometer in the presence and absence of chromium (III) ion. However, the 0.5 μM (500 nM) of Cr<sup>3+</sup> ions was added, the buffer that we used is Britton-Robinson.

## 3. Result and discussion

### 3.1. Characterization of 1-[1-Hydroxy Naphthyl]-6-nitro-2-naphthol-4-sulfonatemodified gold nanoparticles

After synthesized of the HNS-GNPs in optimal conditions (10 ml, 0.0001 M NHS, 10 ml, 0.001 M of HAuCl<sub>4</sub> at 50°C for 3 h), it was characterized by DLS, TGA, TEM,

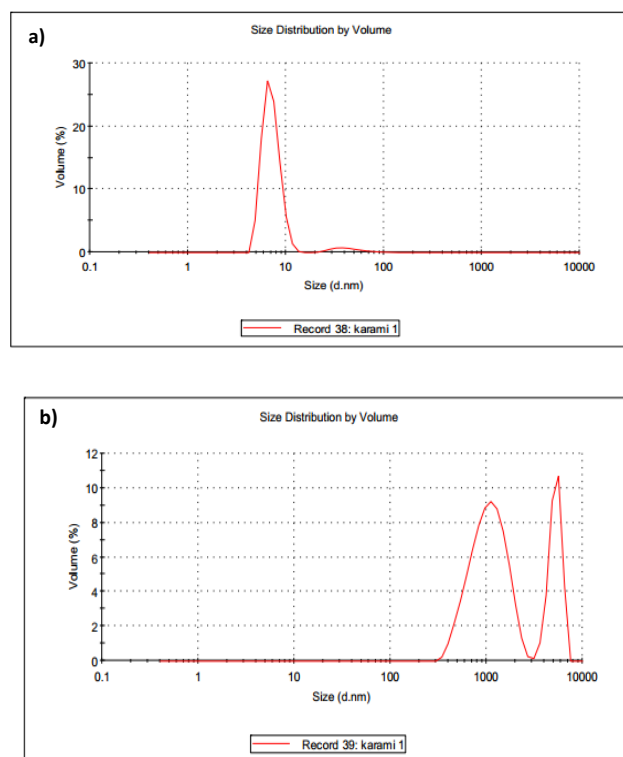


Fig. 1. a) The dynamic light scattering of the HNS-GNPs before adding of Cr<sup>3+</sup> ions, b) The dynamic light scattering of the HNS-GNPs after adding of Cr<sup>3+</sup> ions.

UV-vis spectrophotometer and FT-IR. One of the tools that can show the aggregation of this nanoparticle at the presence of Cr(III) ions is the DLS device which has been shown in Fig. 1a in the absent and Fig. 1b in the presence of Cr(III) ions; some points should be noted with these figures. The diameter of particles has been changed and it has been reached from (Z-Average (d.nm): 46.63) to (Z-Average (d.nm): 802) in the presence of chromium. Therefore, it indicates that aggregation takes place in the presence of Cr(III) ions. The TEM image of as-synthesized HNS-GNPs verified none agglomerated, well dispersed, and uniform spherical with a diameter range of  $25 \pm 5$  nm (Fig. 2). According to previous research by Haiss et al., the maximum absorbance peak of the gold nanoparticle of this range of diameter has shown absorbance maximum in 525 nm [17].

For finding the functionalization of 1-[1-Hydroxy Naphthyl]-6-nitro-2-naphthol-4-sulfonate on the surface of gold nanoparticles, the FTIR spectrum was used. The FT-IR spectra of 1-[1-Hydroxy Naphthyl]-6-nitro-2-naphthol-4-sulfonate ligands are shown in Fig. 3a, the specific peaks of HNS can be seen in  $3446 \text{ cm}^{-1}$ ,  $2823 \text{ cm}^{-1}$ ,  $1340\text{--}1617 \text{ cm}^{-1}$ ,  $1048\text{--}1190 \text{ cm}^{-1}$ , and  $523\text{--}650 \text{ cm}^{-1}$ ; hence, these peaks are added to the FT-IR spectra of gold nanoparticles (Fig. 4b), indicating the interaction of the HNS group with

the surface of the GNPs [18,19]. Finally, TGA shows that a resistant and stable structure has been formed. In this investigation, the weighted powders of HNS-GNPs were carefully recorded by TGA. In Fig. 4, at the  $120^\circ\text{C}\text{--}125^\circ\text{C}$ , the initial weight loss is shown attributed to the physical

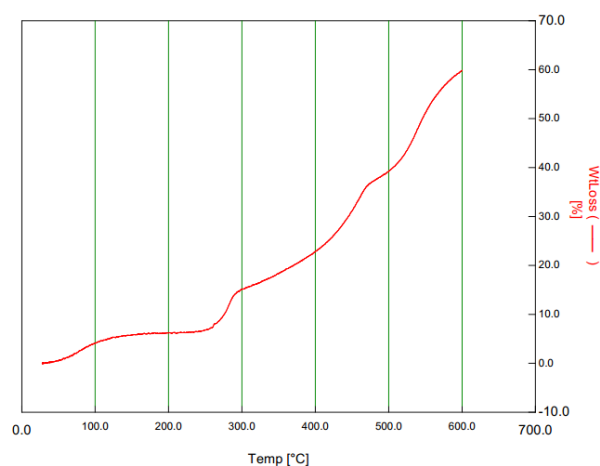


Fig. 4. TGA curves of HNS-GNPs.

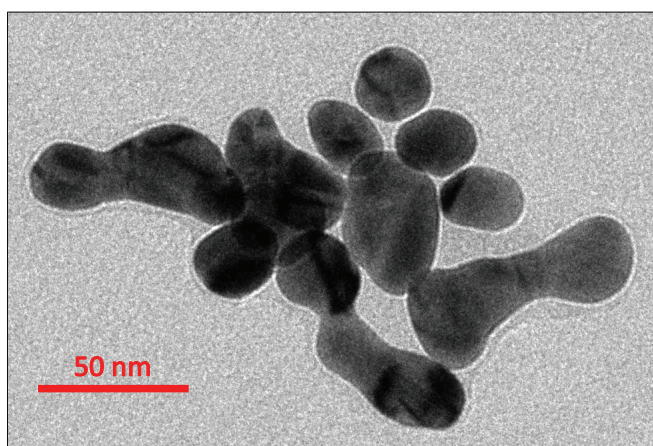


Fig. 2. TEM image of HNS-GNPs with an average size of 20 nm.

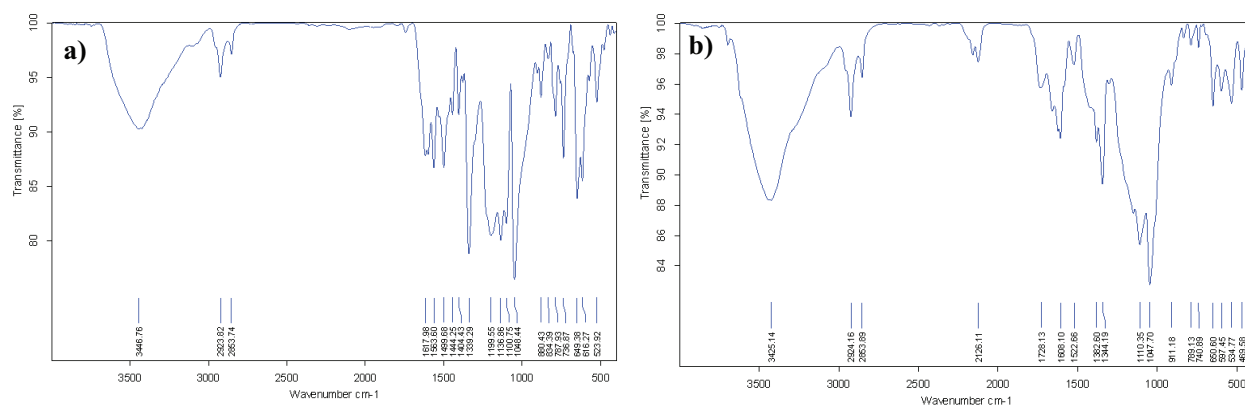
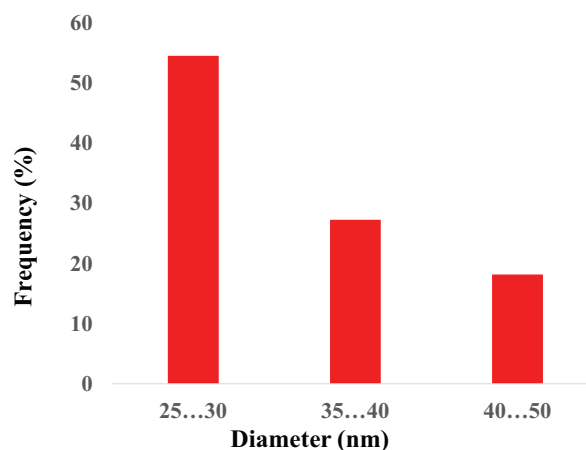


Fig. 3. a) The FT-IR spectra of eriochrome black T, and b) The FT-IR spectra HNS-GNPs.

adsorption of molecules of water in the HNS-GNPs. The other stage, which loses weight in the range of 250–400°C is a considerable amount (%25) due to the decomposition of organic materials or 1-[1-hydroxy naphthyl]-6-nitro-2-naphthol-4-sulfonate on the surface of the gold nanoparticle. The TGA of HNS-GNPs could show a strong interaction of HNS with GNPs.

### 3.2. Selectivity

After synthesis and characterization of HNS-GNPs, as you know well, the GNPs modified with 1-[1-hydroxy naphthyl]-6-nitro-2-naphthol-4-sulfonate is rich of a functional group such as hydroxyl, azo, nitro and sulfonyl which these functional groups were performed strong affinity to metal ions through hydrogen-bonding interaction. In the presence of  $\text{Cr}^{3+}$  in the solution of the functional gold nanoparticle, the interaction between chromium and groups on the HNS-GNPs induced the cross-linking of GNPs, which resulted in appreciable changes in color and absorption properties (Fig. 5). for test the selectivity of our sensor, various ions such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  with concentration (100 nM) were separately added to the HNS-GNPs solution. The values of  $A_{655}/A_{525}$  with these metal ions were remarkable change only in the present of  $\text{Cr}^{3+}$  ions. Therefore, this red wavelength shift of the SPR band is demonstrating that the aggregation happened for HNS-GNPs. These types of interactions are not responsive to other cationic ions (Fig. 6) [7].

### 3.3. Effect of pH

To the effect of pH on detection of  $\text{Cr}^{3+}$  ions in HNS-GNPs solution, the influence of pH in the range of 3–10 in absent and present of  $\text{Cr}^{3+}$  ions was performed. As shown in Fig. 7a, in the range of 3–7 of pH the  $A_{655}/A_{525}$  ratio of HNS-GNPs has low and constant, which means that in this range of pH there is no change in the surface of the nanoparticles or no aggregation in this range occur. The effect of pH on the HNS-GNPs in the present of  $\text{Cr}^{3+}$  is shown in Fig. 7b; the ( $A_{655}/A_{525}$ ) of HNS-GNPs solution in the presence of  $\text{Cr}^{3+}$  was maximum and constant in 5–8 of the pH range. This

indicates that HNS-GNPs were sensitive in this range of pH for the detection of  $\text{Cr}^{3+}$  ions. Because of the chrome ion in the form of a  $\text{Cr}(\text{OH})_3$  colloidal in pH above 5, the  $A_{655}/A_{525}$  ratio was decreased. The pH 5 was chosen to achieve better efficiency.

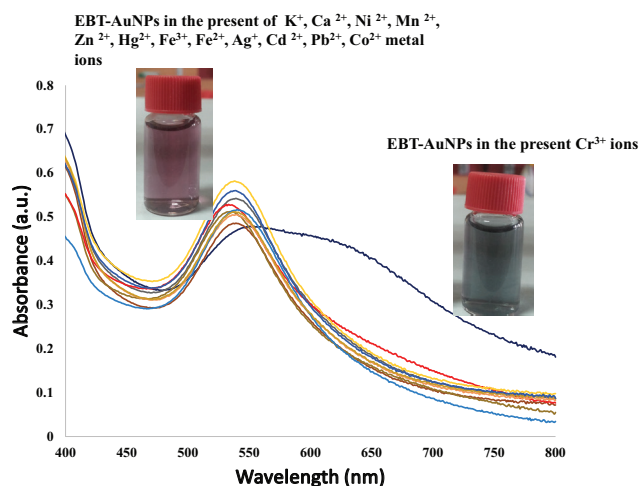


Fig. 6. UV-vis absorption of HNS -GNPs in presence of different metal.

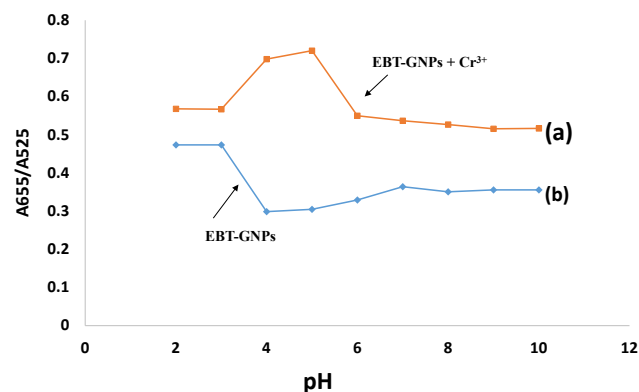


Fig. 7. Influence of pH.

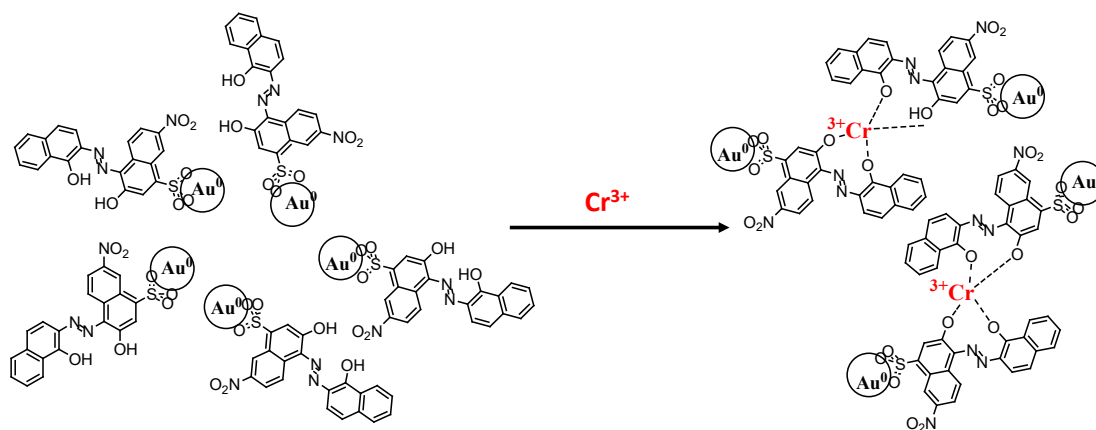


Fig. 5. Plausible mechanism for sensing of chromium by HNS -GNPs.

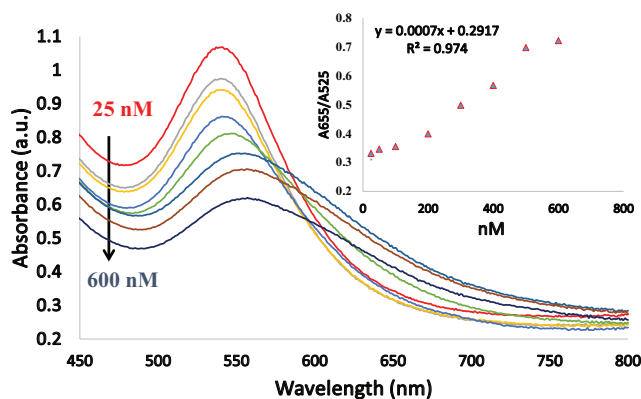


Fig. 8. Change in surface plasmon resonance absorption of HNS-GNPs in the presence of different concentrations from 25 to 600 nM of  $\text{Cr}^{3+}$  ion, pH 5.0, Increase in the relative sensitivity of the detection system with respect to the concentration of the  $\text{Cr}^{3+}$  ions.

### 3.4. The sensitivity

We studied the qualitative and quantitative sensitivity and the detection limit of  $\text{Cr}^{3+}$  ions in an aqueous solution of modified Au nanoparticle. For achieving this goal, various concentration (50 to 600 nM) of the  $\text{Cr}^{3+}$  was added to a solution of the HNS-GNPs at ambient temperature in pH 5.0 (Fig. 8). Moreover, the increase of  $\text{Cr}^{3+}$  ions concentration induced the redshift of the maximal absorption band with a linear relationship ( $y = 0.0007x + 0.2917$ ) and the sensitivity by R is 97% (insert in Fig. 8). One of the points that can be observed by the naked eye, the colour of a solution change from red to blue is observable by adding 100 nM of chromium (III) ions to HNS-GNPs solution. As such, HNS-GNPs can be used for the colourimetric detection of  $\text{Cr}^{3+}$  ions, and the calculated limit of detection (LOD) was about 20 nM according to the  $S/N = 3$  rule. The sensor is available, fast, and straightforward.

### 3.5. Interference studies

To investigate the interference of this method toward  $\text{Cr}^{3+}$  ions, this sensor was challenged with several metal ions, including  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$  (Fig. 9). The SPR of HNS-GNPs in the presence of  $\text{Cr}^{3+}$  change but with other cations were similar to the time that the only the  $\text{Cr}^{3+}$  ions present in the solution. This finding is consistent that the aggregation or the SPR shift of HNS-GNPs is induced in the presence of  $\text{Cr}^{3+}$  ions.

Also, we compared our nanosensor with previous works in Table 1. As stated earlier, a few studies have been reported for  $\text{Cr}^{3+}$  ions that our method is not only simple to synthesis but also it has lower LOD. Besides, to measure  $\text{Cr}^{3+}$  ions, it is acceptable compared to others in terms of sensitivity and LOD [6,20–30].

## 4. Conclusion

The present research reported a simple, facile method for the synthesis of gold nanoparticle capped by available and well-known organic ligand in the lab. In other words, the sensor for detection of Cr(III) with excellent selectivity

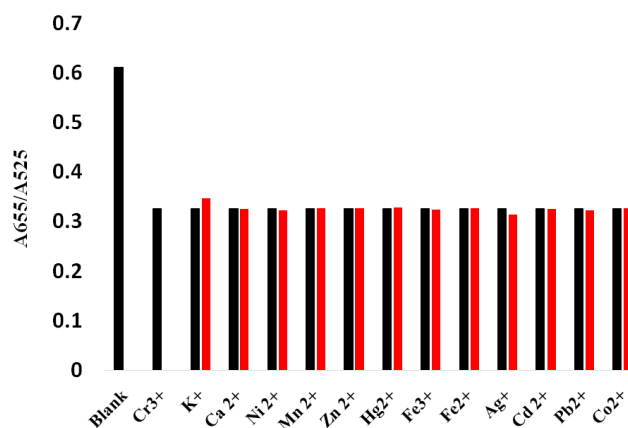


Fig. 9. The  $A_{655}/A_{525}$  ratio of HNS-GNPs the presence of metal ions. Blackbars represent the addition of single metal ion; Red bars represent the mixture of  $\text{Cr}^{3+}$  with another metal ion.

Table 1

Literature reported AuNPs for detecting  $\text{Cr}^{3+}$

Probe	Analyte	LOD	References
DTPA capped gold	$\text{Cr}^{3+}$	0.05 $\mu\text{M}$	6
Borohydride capped gold	$\text{Cr}^{3+}$	0.07 $\mu\text{M}$	20
Tween 20 capped gold	$\text{Cr}^{3+}$	0.016 $\mu\text{M}$	21
Meso-2,3- dimercaptosuccinic acid capped gold	$\text{Cr}^{3+}$	0.01 $\mu\text{M}$	22
EDTA capped gold	$\text{Cr}^{3+}$	0.08 $\mu\text{M}$	23
Citrate capped gold	$\text{Cr}^{3+}$	4.0 $\mu\text{M}$	24
Citrate capped gold	$\text{Cr}^{3+}$	0.022 $\mu\text{M}$	25
Triazole capped gold	$\text{Cr}^{3+}$	1.4 $\mu\text{M}$	26
TNBA-HP capped gold	$\text{Cr}^{3+}$	0.04 $\mu\text{M}$	27
Tripolyphosphate capped gold	$\text{Cr}^{3+}$	0.1 $\mu\text{M}$	28
TNBA capped gold	$\text{Cr}^{3+}$	1 $\mu\text{M}$	29
DTNBA capped gold	$\text{Cr}^{3+}$	0.093 $\mu\text{M}$	30
HNS capped gold	$\text{Cr}^{3+}$	0.05 $\mu\text{M}$	Present work

and sensitivity in aqueous without a need for any harmful organic solvent and with the detection limit of 20 nM is introduced.

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