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Detection of copper ions using modified gold nanoparticles by two-functional groups

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ABSTRACT

In this study, gold nanoparticles were fabricated using two different functional groups such as crown ether and carboxylic acid and evaluated as a sensor to detect copper ions in an aqueous solution. The Au-crown/carboxylic is characterized with TEM, FTIR spectroscopy. To compare the response of the sensor to copper ions, the UV-vis spectrum was characterized before and after the increase of Cu^{2+} ions. The mechanism to be considered for measuring copper ions in aqueous solutions is that Cu^{2+} ions can successfully complexation with Au-crown/carboxylic which comes with color changes from red to blue. In the range of 75 nM to 1250 nM, the link between the decrease in adsorption intensity and the concentration of Cu^{2+} ions at A630/A545 is linear with 0.9814 and 150 nM correlation coefficient and the limit of detection, respectively. In other words, among several other cations, the sensor assay especially measures copper ions and also has very simple and able to measure and detect copper ions in an aqueous solution.

Keywords: Nano probe, sensor, crown ethers, carboxylic acid, copper (II)

1. Introduction

One of the most significant problems for researchers is the contamination of drinking water by heavy metals [1]. However cupper is one of the necessary elements for plants and animals but, its large amount is toxic for all creatures. Toxication with Cu^{2+} results in the headache, heart beats, kidney damage, liver diseases, hair falling, intestinal problems and anemia [2]. Several ways for the detection of heavy metals ions in different samples have been reported such as voltammetry [3], ICP-AES [4], ICPMS) [5], and AAS [6].

The simplicity and high sensitivity of nanoparticles as colorimetric assays have recently attracted increasing attention. Among the nanomaterials that are easily synthesized and applied, gold nanoparticles have a high molar extinction coefficient and are mostly used for colorimetric purposes of various targets [7,8], e.g. DNA [9,10], molecular Sensors [11], biosensors Based on Aptamers [12], peptide [13], proteins [14,15] and metal ions [16]. The SPR is interesting properties because of can be ordered by changing its shape and size [17]. Gold nanoparticle-based color sensors, which result from the association between particle plasmon and nanoparticle aggregation, change color from red to blue, which can be used for analysis [18,19].

Here we present highly sensitive and selective probe for detection of copper (II) with colorimetric in aqueous solution and the gold nanoparticles synthesized in this study were modified with two different functional groups that enhance its ability to measure elements. (Scheme 1). the Au-crown/carboxylic nanoparticles was characterized by FT-IR, Uv-Vis spectrophotometer, TEM. The proposed mechanism for measuring copper ions forms a complex with each of the two or more modified copper ores, which causes the particles to come together and increase in diameter as the radius increases. The proposed mechanism for measuring copper ions is that with each copper ion with two or more modified gold nanoparticles form a complex, which causes the particles to aggregate and increase the diameter of the particles as a result the absorption wavelength has changed at A630/A545.

2. Experimental section

2. 1 Instruments

The transmission electron microscopy (TEM) images were recorded by a Philips EM 208, at 100 kV. The FTIR spectra were recorded on Bruker (TENSOR 27) in range 400-4000 cm^{-1} wavenumber into KBr pellets. UV-vis spectrometer was recorded

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on Cary 100 UV-Visible, PH meter model 827, produced by Metrohm, with an accuracy of 0.001 for pH, 6-liter ultrasonic bath model Elma (S60H) made in Germany.

2. 2 Materials

High purity materials were used in the experiment. Hydrogen tetrachloroaurate (III) ($HAuCl_4.4H_2O$, 99.99%), trisodium citrate dehydrate ($C_6H_5Na_3O_7$-$2H_2O$), L-cysteine ($C_3H_7NO_2S$), tetra methyl ammonium hydroxide (TMAOH), Benzo-15-crown-5-ether, Phosphoryl chloride ($POCl_3$), Salts of the different cations studied ($B(NO_3)_3$, $BaCl_2$, $FeCl_3$, $AgNO_3$, $Pb(NO_3)_2$, $CoCl_2$, $Cr(NO_3)_2$, $MnCl_2$, Hg_2Cl_2, $Hg(NO_3)_2$ and $CuCl_2$).

2. 3 Synthesis of Au-nanoparticles

Briefly, the solution of $HAuCl_4$ (0.001M) was heated until 80 ◦C and stirred vigorously for 20 min then sodium citrate solution (15 mM, 100mL) was added drop by drop. Within this stage the black solution changed to reddish-brown gradually. After heating for extra 1 h., the reaction mixture was cooled and collected [20].

2. 4 Synthesis of Au-cysteine nanoparticles

The obtained Au-nanoparticles (100 mg) was dispersed in ethanol (50 mL) and treated by ultrasonic for 30 min. After homogenizing the solution, cysteine (5 mL× 10^{-3} M) was added and stirred for 24h at room temperature. In this method, due to the fact that L-cysteine has thiol groups, citrate replaces with thiol of L-cysteine well on the surface of gold nanoparticles and forms a strong bond [21].

2. 5 Synthesis of Au-crown/carboxylic

Dissolve the benzo-15-crown-5-ether (1 mmol) in 5 mL DMF and the mixture was cooled to -5℃, then phosphoryl chloride ($POCl_3$) (1 mmol) was added dropwise to the mixture. The mixture stirred at room temperature for about 1 h, then the reaction mixture was refluxed for 4 h. After cooling, it poured carefully onto ice. Product was dissolved in ethanol and then the mixture was added dropwise to Au-crown/carboxylic nanoparticles. The reaction mixture was refluxed in N_2 atmosphere for two days. After nanoparticles were washed in ethanol and water, the product was dried.

2. 6 The Cu^{2+} ions colorimetric determination

For colorimetric detection of copper(II) ions, the metal ions such as Ba^{2+}, Hg^{2+}, B^{+}, Hg^{+}, Co^{2+}, Ag^{+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Cr^{2+} and Fe^{3+} at the same concentration (200 nM) and the same conditions were added into 1.00 mg Au-crown/carboxylic. The changing in the UV/vis spectrum (A630 / A545) are monitored at room temperature

2. 7 The colorimetric detection of Cu^{2+} ions

Different concentrations of Cu^{2+} with stirred at room temperature add to 0.33 mg/mL of Au-crown/carboxylic then stirred for 10 min, Record the absorption spectrum using a spectrophotometer and the concentration of Cu^{2+} ion to the ratio of absorbance of Au-crown/carboxylic at (A630/A545) was plotted.

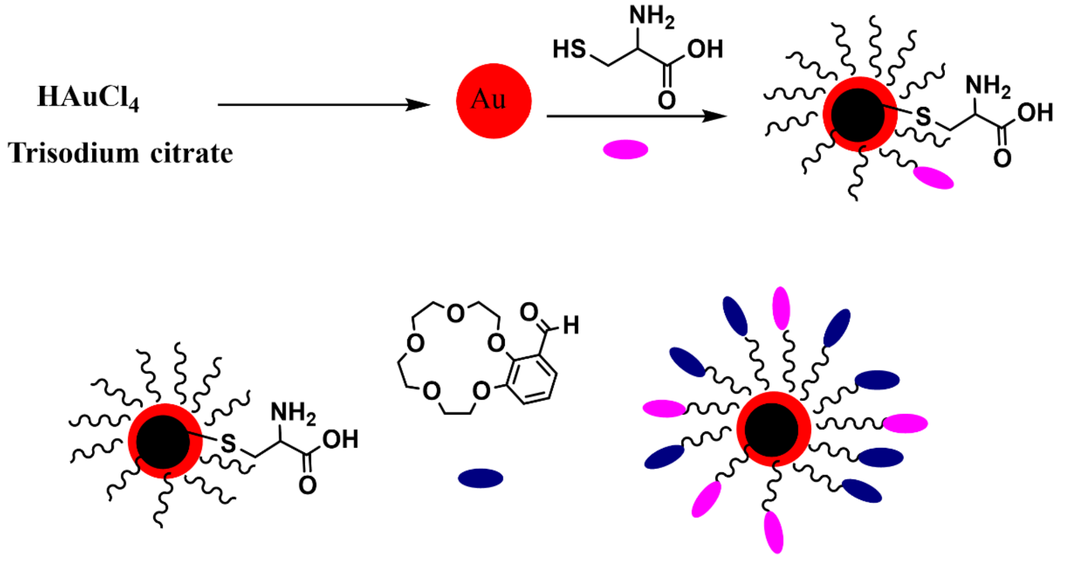
2. 8 The effect of pH

Au-crown/carboxylic were added with Cu^{2+} 1mL ions in 2.0 mL aqueous solution (10 millimolar [mM] buffer). The Britton-Robinson as a buffer and the pH value are in the range of 2 to 12

3. Results and Discussion

3. 1 Synthesis of Au-crown/carboxylic

First, the synthesis of Au-crown/carboxylic was planned through the pathways shown in Scheme 1. Au is the soft acid and cysteine is soft bases (donor), therefore a strong covalent bond (Au-SR) occurs between Au and cysteine. Eventually, the N-terminal cysteine residues to react with ether crown aldehyde group to give imines [22]. Due to the fact that the carboxylic acid functional group is present in the cysteine ligand, so by placing crown ether on the surface of gold nanoparticles, it is modified with two groups.



Scheme 1: Synthesis of Au-crown/carboxylic ligand.

Synthesized Au-crown/carboxylic were characterized by FTIR spectrum, UV-Vis absorption spectrum and transmission electronmicroscopy (TEM). Fig. 1 shows the UV–Vis absorption spectrum of Au-crown/carboxylic nanoparticles that the SPR at 545 nm is a clear evidence of synthesis of Au-crown/carboxylic nanoparticles [20].

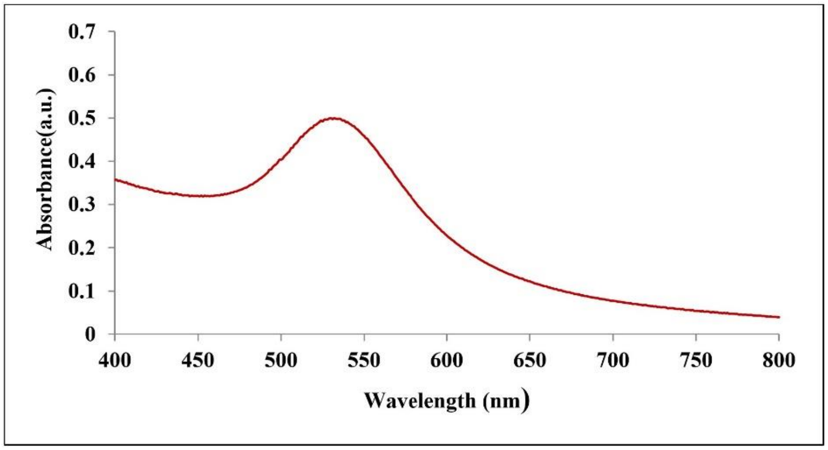


Figure 1: The UV–Vis absorption spectrum of Au-crown/carboxylic nanoparticles.

The **Fig. 2a** shows the TEM image of Au-crown/carboxylic nanoparticles that the images indicate Au-crown/carboxylic nanoparticles and **Fig. 2b** shows the histogram of 100 randomly selected nanoparticles, so, most of the particles are between 1 and 5 nanometers, which is 50% of the total particles. It is obvious that synthesized NPs have an almost uniform size and there is not more dispersion.

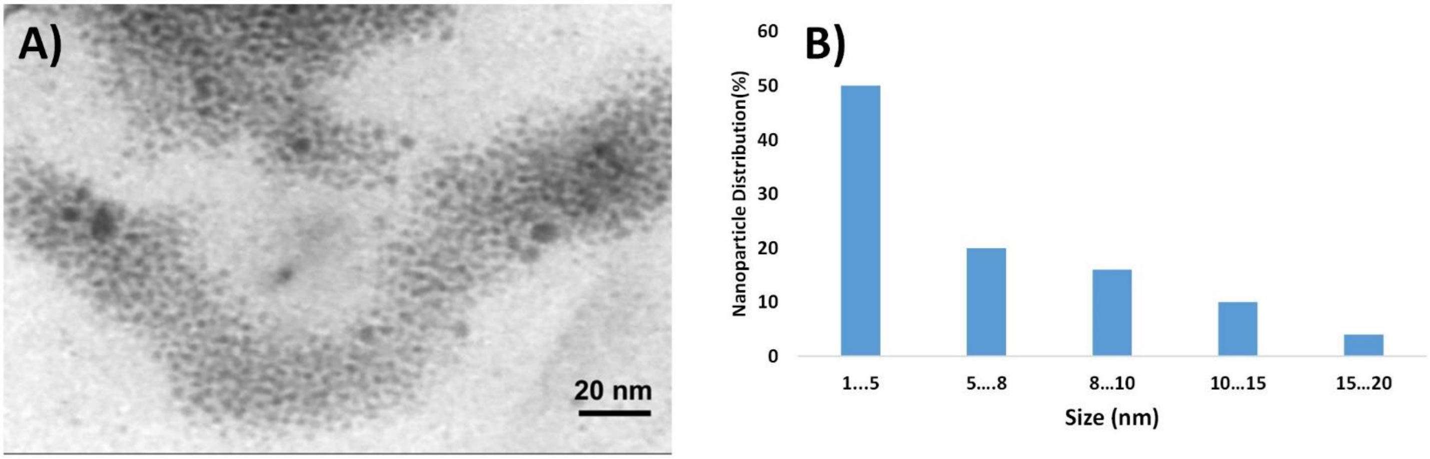


Figure 2: A) The TEM image of Au-crown/carboxylic nanoparticles with 20 nm scale bar, B) the histogram of 100 randomly selected nanoparticles

The FTIR spectra of Au-crown/carboxylic are presented in **Fig.3**. The signals observed at 3395 and 1731 cm^{-1} corresponds to OH stretch and the carbonyl stretch of a carboxylic acid group, in addition, two bands observed at 2977 cm^{-1} and 2841 cm^{-1} related to C-H and 1625 cm^{-1} correlated to C=N stretching vibrations Au-crown/carboxylic.

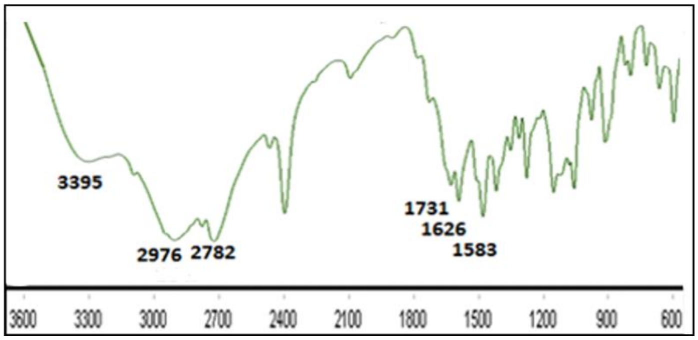


Figure 3: FT-IR spectra of Au-crown/carboxylic

3. 2 Metal ions sensing ability of Au-crown/carboxylic

As mentioned above, Au-crown/carboxylic nanoparticles display obvious SPR. The SPR can be easily affected by various external factors, such as aggregation [23,24]. To investigate the various metals ions diagnosis ability of Au-crown/carboxylic nanoparticles, the same concentration of metal ions (200 nM) were added the solution of Au-crown/carboxylic (4 mL). The **Fig. 4** shows the SPR of Au-crown/carboxylic with metal ions. According to figure, which is based on A630/A545 absorbance ratio, this nano probe is so sensitive to copper than other elements.

Crown ethers are known for their strong tendency to form complexes with metals ions and most of these compounds have been used to identify specific metal ions [25,26]. In the other words, Crown ether are known for the unusual property of forming stable complexes with metal ions. Upon complexation with Cu^{2+} ions, the aggregation was happen in the surface of nanoparticles, so it is the best condition for Au-crown/carboxylic which leads to an increase in particles size. Therefore, it causes to change SPR or A630/A545 absorbance ratio. In this study, with aggregation in the surface of nanoparticles, the SPR or A630/A545 absorbance ratio was decreased, and the sediment of gold nanoparticle in the presence of Cu^{2+} ions due to aggregation is the reason of this decreasing [27,28].

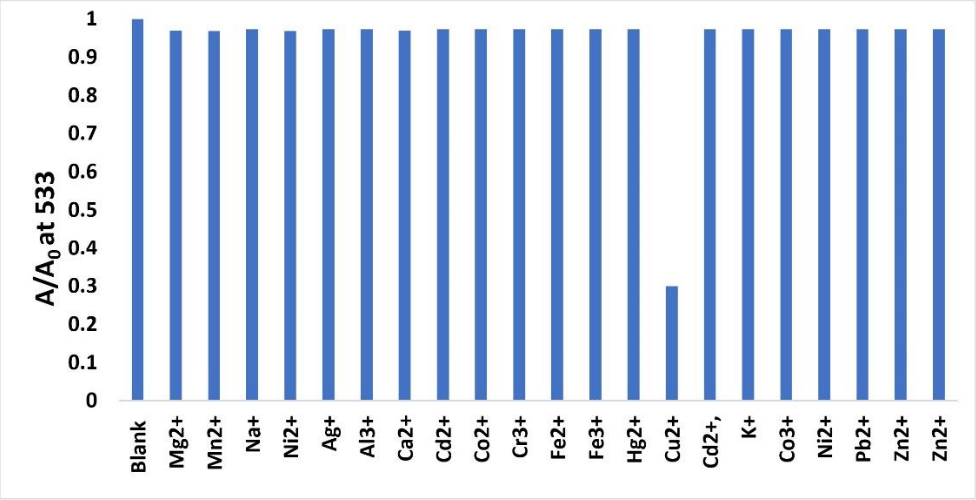


Figure 4: The UV–vis absorption of Au-crown/carboxylic in presence of different metal ions with same concentration (200 nM) in 10 min and 25 °C

3. 3 Effect of pH

Optimal sensor conditions need to be studied for better performance. The effect of pH on absorbance spectrum and the absorption ratio of 1.00 mg Au-crown/carboxylic in the presence of Cu^{2+} solution (200 nM) in 10 min and 25 °C show in the **Fig. 5**. The A630/A545 of Au-crown/carboxylic was constant and low in the pH range 4-8, so, it indicates that Au-crown/carboxylic were stable in these range of pH. The absorbance ratio (A630/A545) of Au-crown/carboxylic significantly increased in pH range 9-11. As you well known, the heavy metals at pH> 9 is precipitated as metals hydroxide insoluble [29], so we chose the pH at 7 range in this pH the A630/A545 ratio is the lowest value.

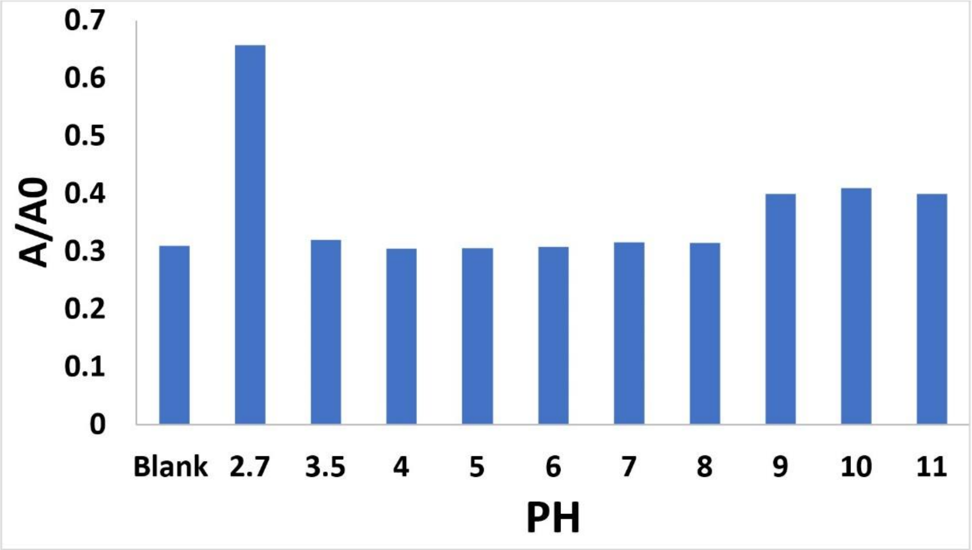


Figure 5: The effect of pH on the absorption ratio of 1.00 mg Au-crown/carboxylic in the presence of Cu2+ solution (200 nM) in 10 min and 25 °C

3. 4 Nano sensor evaluation

For evaluation, the sensitivity of this sensor for Cu^{2+} detection, different concentrations of Cu^{2+} of ranging from 75 to 1250 nM were used to this system. The Fig.6 shows changes in A630/A545 absorbance ratio with the addition of different concentrations Cu^{2+} ions to 1.00 mg Au-crown/carboxylic in 10 min and 25°C. The A_{630}/A_{545} absorbance ratio decreased with increasing Cu^{2+} ions concentration. There is a linear relation between A630/A545 absorbance ratio and copper concentration in the range 75-1250 nanomolar (nM) with a calibration equation of $y=0.0005x+0.9593$ ($r = 0.9814$). The detection limit (S/N ratio of 3) and sensitivity were 150 nM and LOQ was calculated 500 nM. The Table 1 shows the linear range calibration sensitivity and detection limit of this sensor for copper determination. As it is shown, these factors are comparable and even better than those have been reported for other sensors [30-32].

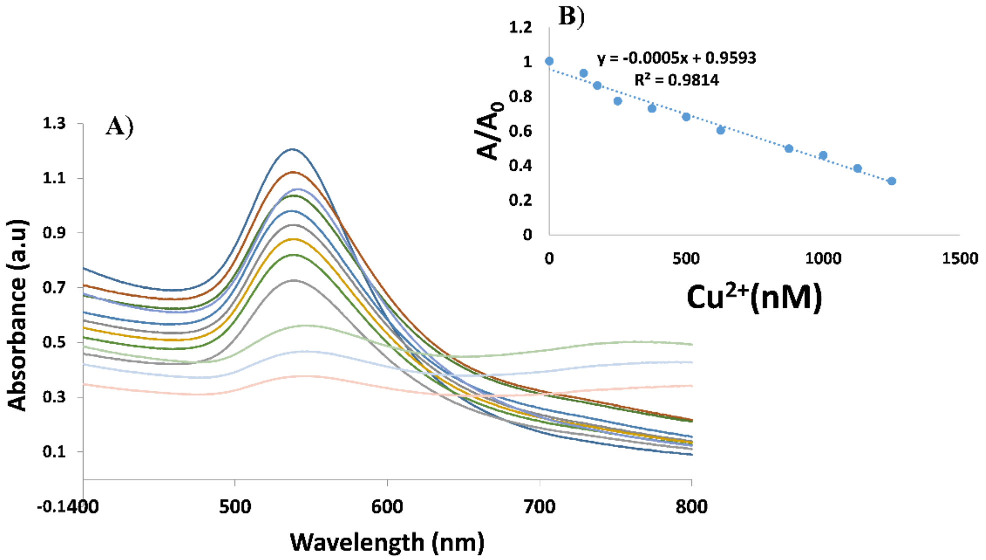


Figure 6: A) Change in surface plasmon resonance absorption of Au-crown/carboxylic in the presence of different concentrations from 75 to 1250 nM of Cu2+ ion, pH 7.0, **B**) decrease in the relative sensitivity of the detection system with respect to the concentrat

Table1 : A comparison of various colorimetric assays for Cu2+ ions

Entry	Probe	LODs	Target	Refs
2	unmodified gold nanoparticles	10- 0.1μM	Cu^{2+}	[30]
1	Protein- AuNPs	200 nM	Hg^{2+}, Pb^{2+} and Cu^{2+}	[31]
3	Pyridines- AuNPs	----	Cu^{2+} and Ag^{+}	[32]
4	Au-crown/carboxylic	150 nM	Cu^{2+}	this work

3. 5 Interference studies

To check the selectivity of this sensor toward Cu^{2+} over other cations UV-Vis spectra of Au-crown/carboxylic nanoparticles modified in the presence of other metal ions containing Mg^{2+}, Mn^{2+} ,Cr^{6+}, Co^{3+}, Ni^{2+}, Pb^{2+}, Na^{+}, Ni^{2+}, Ag^{+}, Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Cd^{2+}, K^{+} and Zn^{2+} were recorded. As demonstrated in **Fig.7**. The value of A_{630}/A_{545} for to the mixture of Cu^{2+} with another metal ions was almost equal with Cu^{2+} ions. This shows that other metal ions did not interfere in the binding of Au-crown/carboxylic with Cu^{2+} ions.

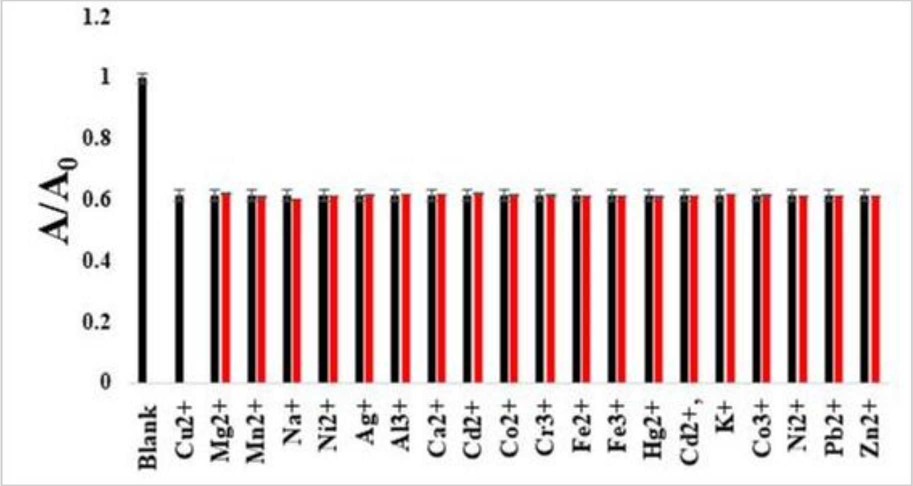


Figure 7: Absorbance ratio (A/A0) of Au-crown/carboxylic in the presence of metal ions. Red bars represent the addition of single metal ion; Blue bars represent the mixture of Cu2+ with another metal ions

3. 6 Real samples

To explore the applicability, the Au-crown/carboxylic in an analysis of Cu^{2+} ions in real samples including tap water was analyzed using the standard addition protocol [33-35]. As shown in **Table 2**, the recovery percentages of the spiked samples were in the range of 98.0–104.3% at admissible RSD values. Based on the results, the Cu^{2+} ions has a potential application in detection of Cu^{2+} ions in real water samples.

Table 2: Determination of concentration amounts of Cu2+ ions in water samples (n = 5).

Sample	Added (nM)	found (nM)	Recovery (%)	RSD%
1	0	-	-	-
2	100	9.8	98	3.02
3	500	501.6	100.3	2.06
4	1000	104.3	104.3	5.75

4. Conclusion

In this research, a sensitive and selective method for the identification of copper ions based on colorimetric assay was designed by modifying the surface of gold nanoparticles by crown/carboxylic. Although Au-crown/carboxylic have a several advantages similar to other nano sensors first of all it is very sensitive with low detection limit and also is very easy to synthesis. In addition to, the crown ether in the surface of the Au-crown/carboxylic is appropriate for complexation with Cu^{2+} ions. The complexation of Au-crown/carboxylic with Cu^{2+} will lead color and spectral change. Therefore, these changes in the adsorption and color of the nanoparticle solution can be related to the concentration of copper ions added and it can be easily detected in solutions and its exact value can be calculated. This method is a very useful and accessible method because it does not require complicated sophisticated equipment with high sensitivity and acceptable detection (LOD of 150 nM), that this amount is much lower than the maximum acceptable concentration of Cu^{2+} ions in water and drinking water. The results obtained and the impressive properties of the nano sensor make this proposed method, which is simple, fast and reliable, suitable for measuring the concentration of Cu^{2+} ions in an aqueous solution.

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