

Synthesis of SPR Nanosensor using Gold Nanoparticles and its Application to Copper (II) Determination

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Abstract This research describes a colorimetric assay for Cu (II) ions that is highly selective over other metal ions. It is based on the measurement of changes in the surface plasmon resonance absorbance (at 525 nm) of gold nanoparticles (Au NPs) modified with 1,7-diaza-15-crown-5 (Crown-Au NPs). The unique structure of crown ethers and presence of heteroatoms enable the crown-Au NPs to recognize very low concentrations of Cu (II) ions. After aggregation, the surface plasmon absorption band has a red shift so that the nanoparticle solution shows a violet color. The TEM images data show that this color change is a result of crown-Au NPs aggregation upon addition of Cu (II). In contrast, other metal ions Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Ag^{+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^{+} , Mg^{2+} , Mn^{2+} , Na^{+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} do not aggregate. The recognition mechanism is attributed to the formation of a sandwich (2+1) between the Cu (II) ion and two diaza-15-crown-5 moieties that are attached to separate nanoparticles. This simple and fast method can be used to determine the Cu (II) ions with a detection limit as low as 200 nM.

Keywords Gold nanoparticle · 1,7-diaza-15-crown-5 · Sensors · Nanoparticles · Colorimetric sensing · Cu^{2+}

1 Introduction

Recently, there are very active researches in analytical chemistry synthesizing and studying noble metal nanoparticles sensing properties. Hence, many applications become possible by using metal NPs as probes for various analysis assays [1]. Meanwhile, the development of NPs-based approaches for the detection and screening of biomolecules is an important and highly active research field because of the scientific and practical significance of miniaturized analytical tools.

Toxic metals determination is an important issue in both environmental monitoring and clinical research. Copper ions are an essential element for electron-transfer reactions in various biological processes [2]. At elevated concentrations, it is highly toxic to organisms such as algae, fungi and many bacteria, and in humans may adversely affect the gastrointestinal and hepatic functions [3, 4]. For example, the detection and measurement of copper ions in water is useful for scientists. Several analytic methods such as atomic absorption spectrometry [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], and electrochemical methods have been developed [7] to identify and detect the Cu^{2+} ions. However, these methods and many other ones often require quite expensive and time-consuming sample pretreatment including pre-concentration and matrix separation. Among the reported methods, colorimetric chemosensors, especially gold nanoparticles (AuNPs), have been extensively utilized for their simplicity and ease of observation using the naked eye without requiring complicated instrumentation [3, 8, 9].

In the last decade, gold nanoparticles (AuNPs) have become highly studied materials and been widely used in a range of applications including: sensing, electronics, and surface enhanced Raman spectroscopy. Surface plasma res-

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onance (SPR) absorption of AuNPs is extremely sensitive to their size, shape, surrounding media and inter-particle distances. In particular, the distance-dependent optical properties of AuNPs have been extensively employed as the analytical probes in biotechnological and chemical systems, such as colorimetric sensors for metal ions [10–14], ions [15], and other analytes [12–20]. In these assays, analyte-triggered aggregation of AuNPs leads to a red shift in the SPR absorption band resulting in a red-to-blue color change. The distance-dependent SPR absorption of Au NPs has become a useful tool for the colorimetric sensing development of various analytes.

In this paper, a simple colorimetric system is performed to detect Cu^{2+} using 1,7-diaza-15-crown-5 functionalized gold nanoparticles (crown-Au NPs). When Cu^{2+} is added to the solution, its color changes from brown to violet which is a result of the aggregation via the simple host-guest interactions between Cu^{2+} ions and two 1,7-diaza-15-crown-5 moieties (Scheme 1).

2 Experimental Section

2.1 Materials

The compounds dodecanethiol, hydrogen tetrachloroaurate (III), tetraoctylammonium bromide and 11-mercaptoundecanoic acid are obtained from Sigma-Aldrich. In addition, kryptofix (1,7-diaza-15-crown-5), sodium borohydride, and trifluoromethanesulfonic acid (Tf_2O) were purchased from Merck. All different cations, in the form of nitrate or chloride salts including $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$, KNO_3 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, AgNO_3 , $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were also purchased from Merck. Doubly distilled water was used in the experiments,

and the glassware was washed with ($\text{HCl}:\text{HNO}_3 = 3:1$ (v/v)) and well rinsed with MilliQ water prior to use.

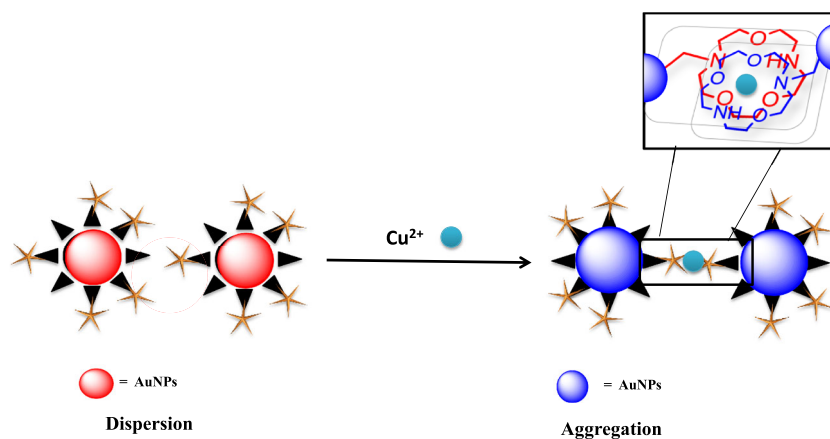
2.2 Instrumentation and Synthesis of Modified Gold Nanoparticles

Absorption spectra were taken on a Cary 50 at room temperature, and High-Resolution Transmission Electron Microscopy was carried out on a Philips, CM30, 300 KV, and ultrasonic Sonorex Digitec 255H. Infrared spectra were obtained on a Bruker, Tensor 27 FTIR Spectrometer. Samples were pressed into KBr pellets and results are reported in wave numbers (cm^{-1}). Synthesis is performed via a modified Brust method as described previously [21] using octanethiol (2.7 mmol) as ligands for nanoparticles preparation in the course of gold reduction with sodium borohydride. Nanoparticles are purified by precipitation and centrifugation using a mixture of ethanol/acetone, ethanol, and AuNPs are dispersed in toluene and stored in the dark. In the next step, The MUA-AuNPs are prepared by dissolving 50 mg, 0.06 mmol of the AuNPs in 10 mL tetrahydrofuran and then 40 mg, 0.18 mmol of 11-mercaptoundecanoic acid is added. Finally, the mixture is stirred at room temperature for 6 hours [22].

2.3 Synthesis of 1,7-diaza-15-crown-5 Functionalized Gold Nanoparticles (crown-AuNPs)

The crown-AuNPs are prepared by dissolving 40 mg, 0.05 mmol of the MUA-AuNPs in 10 mL dichloromethane and then 70 mg, 0.25 mmol of trifluoromethanesulfonic anhydride (Tf_2O) is added. In this step, the mixture is stirred at room temperature for 10 min. Afterwards, 65 mg, 0.24 mmol of the 1,7-diaza-15-crown-5 is added to the mixture, and the mixture stirred at room temperature for 30 min. The solvent is removed via rotary evaporation and washed copiously with water and acetone (3:7, v/v) to remove the unreacted starting materials [17].

Scheme 1 Schematic illustration of the analytical process for detecting Cu^{2+} based on the aggregation of crown-AuNPs



2.4 Colorimetric Assay

Different metal ions of each metal ion (100 μM): Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Cd^{2+} , K^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} are added separately to a 3.0 mL THF solution containing crown-AuNPs. The mixtures are maintained at room temperature for 30 min, and then their SPR absorption bands are recorded by a UV–Vis spectrophotometer. A significant change in spectra with distinct red-to-blue color change was noted in the Cu^{2+} case, whereas for the other metal ions almost negligible change was observed.

2.5 The Influence of pH on Cu^{2+} Induced Aggregation of 1,7-diaza-15-crown-5-AuNPs

The Cu^{2+} ions (100 μM) were added to 0.2g of the crown-AuNPs dissolved in 3 mL of THF/ H_2O (3/7) and 0.5 mL, 0.02 M of buffer so that the buffers were: pH 2–12, Britton-Robinson buffer.

3 Results and Discussion

3.1 Surface Modification of AuNPs with 1,7-diaza-15-crown-5

The synthesis of 1,7-diaza-15-crown-5 functionalized gold nanoparticles (crown-AuNPs) was planned as shown in Scheme 2.

At first, synthesis was carried out via a modified Brust method as described previously [21] using octanethiol as ligands for nanoparticles preparation in the course of gold reduction with sodium borohydride. In the next step, according to the Murray model for the place exchange reaction, an excess amount of 11-mercaptoundecanoic acid is used as the incoming ligand [22]. Eventually, 1,7-diaza-15-crown-5 functionalized gold nanoparticles (crown-AuNPs) are synthesized in the presence of Tf_2O .

3.2 Characterization of Crown-AuNPs

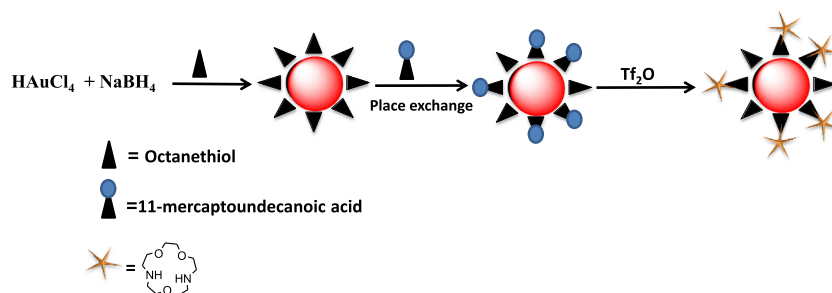
Transmission electron microscopy (TEM) images reveal that the average particle size of crown-AuNPs is around

1.5 ± 0.5 nm (Fig. 1). The UV–Vis spectrum also shows that the plasmon frequency depends strongly on the particle size and plasmon frequency is clearly absent for nanoparticles smaller than 2 nm [23]. The presence of crown-AuNPs was also verified by infrared spectroscopy, and Fig. 2a shows the infrared spectroscopy of AuNPs. In addition, for the FTIR spectrum of MUA-AuNPs, the modes of MUA-AuNPs at 1638 cm^{-1} can be attributed to the C=O stretching vibration of $\nu(-\text{COOH})$, and the bands at 2974 cm^{-1} and 2924 cm^{-1} can be assigned to C–H stretching vibrations. The hydroxyl of the carboxylic acid group peak is seen about 3444 cm^{-1} (Fig. 2b). In Fig. 2c, the absorption peaks at 3445 , 2919 , 2848 , 1706 , 1409 , and 1191 cm^{-1} are observed for MUA-AuNPs, and a new peak is also observed at 1513 and $3700\text{--}3500\text{ cm}^{-1}$ corresponding to the amide group of crown-AuNPs. These results indicate that the 1,7-diaza-15-crown-5 is successfully linked to the surface of MUA-AuNPs via the Tf_2O reaction.

3.3 Metal ion Selectivity of crown-AuNPs

The sensing ability of crown-AuNPs is tested with various metal ions in THF/ H_2O solution. The UV–Vis spectra of the synthesized 1,7-diaza-15-crown-5-AuNPs are measured in the presence of metal ions such as Fe^{2+} , Fe^{3+} , Hg^{2+} , Ag^+ , Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . The Cu^{2+} ion is the only ion that has a plasmon absorption peak in the UV–Vis spectra (Fig. 3a), the ratio value of A_{600}/A_{525} is significantly higher than those of the other metal ions (as shown in Fig. 3b). All that is mentioned above indicates that the crown-AuNPs have a selective response towards the Cu^{2+} ion. In other words, the transition of nanoparticles from dispersion to aggregation exhibits a distinct change in color, and this is due to the coupling of the plasmon absorbance as a result of their proximity to each other [24]. The other metal ions do not influence the absorption spectra indicating that no aggregation occurred. The 1,7-diaza-15-crown-5 on the surface of AuNPs functions as a metal ion chelate. The Cu^{2+} ions are binding with two 1,7-diaza-15-crown-5 via simple host-guest interactions on the surface of a gold nanoparticle as a sandwich induced by the aggregation of the crown-AuNPs (Scheme 2). Fig. 1b shows a TEM image

Scheme 2 Schematic illustration of synthesis and assembly of crown-AuNPs



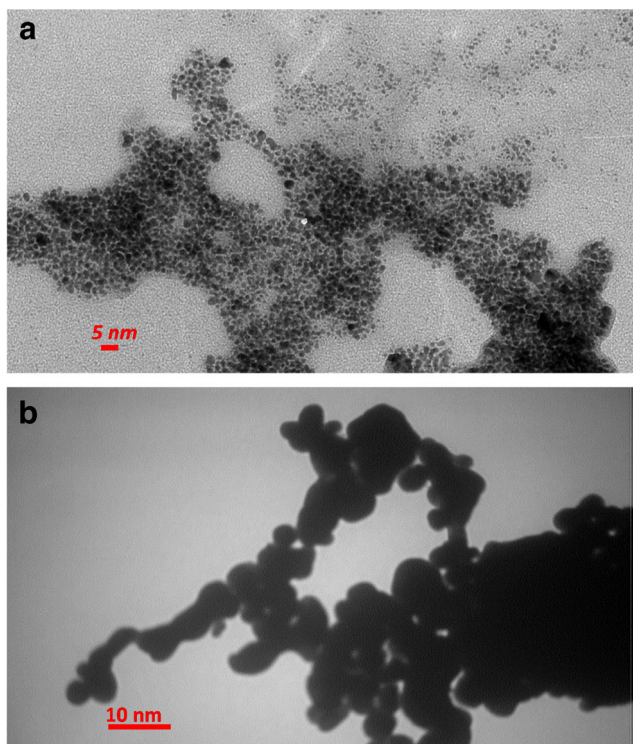
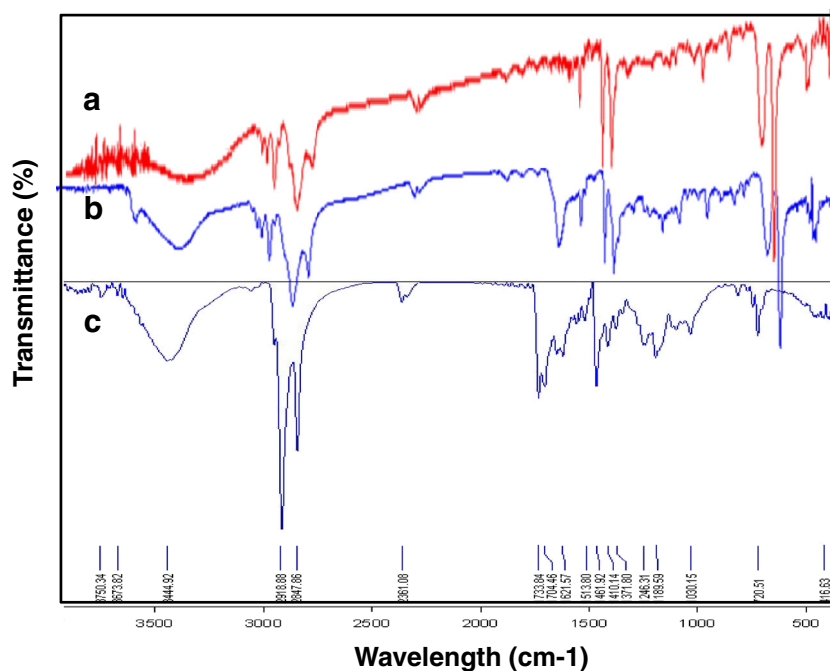


Fig. 1 **A** TEM image of crown-AuNPs average particle size around 1.5 ± 0.5 nm, **B** TEM image of crown-AuNPs in the presence of Cu^{2+} ions average particle size around 10 ± 3 nm

of the Cu^{2+} -induced aggregation of crown-AuNPs so that the gold particle size is 10 nm in the presence of the Cu^{2+} ions.

Fig. 2 FTIR of **A**) AuNPs, **B**) MUA-AuNPs, and **C**) crown-AuNPs



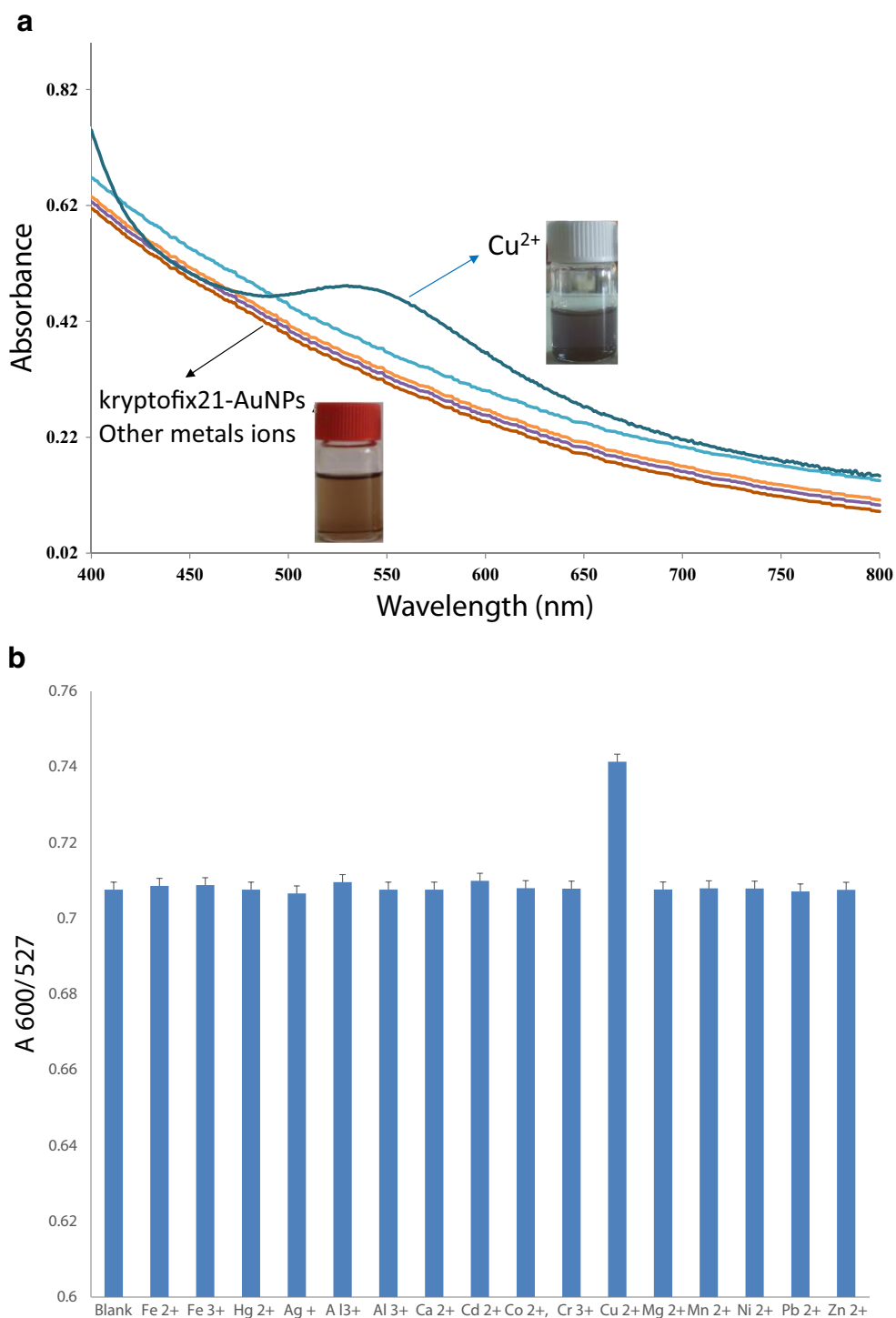
3.4 The Influence of pH on Cu^{2+} -induced Aggregation of 1,7-diaza-15-crown-5-AuNPs

The pH titration of crown-AuNPs is carried out to investigate the pH range in which crown-AuNPs can effectively detect Cu^{2+} . In Fig. 4a, the absorbance ratio (A_{600}/A_{527}) of 1,7-diaza-15-crown-5-AuNPs is low and constant in the pH range 3–11. This indicates that crown-AuNPs are stable in this wide pH range. The influence of pH on Cu^{2+} -induced aggregation of crown-AuNPs is shown in Fig. 4b; addition of Cu^{2+} resulted in a high absorbance ratio (A_{600}/A_{527}) at pH 4–10. Therefore, the optimal pH range for detecting Cu^{2+} by crown-AuNPs is in this pH range.

3.5 Colorimetric Assay of Cu^{2+} ions

The aggregation degree of crown-AuNPs depends on the concentration of the Cu^{2+} ion. The Cu^{2+} ion is added into crown-AuNPs solutions containing B-R buffer at pH 6–7 at room temperature which is monitored with the UV–Vis absorbance values in Fig. 5a. The SPR absorption ratios (A_{600}/A_{527}) change and have a red shift with the addition of different concentrations of Cu^{2+} ion, and a linear relationship has been found when the concentration of Cu^{2+} ions is between $10 \mu\text{M}$ and $250 \mu\text{M}$. The increase in SPR during Cu^{2+} titration is due to the induced aggregation of crown-AuNPs, so the detection limits are found to be $0.2 \mu\text{M}$ or (200 nM) for Cu^{2+} on the basis of a signal-to-noise ratio of 3:1, and correlation coefficients (R^2) 0.9604 (Fig. 5b).

Fig. 3 **A** UV–vis spectra of crown-AuNPs in the presence of various metal ions (100 μ M) and color change upon addition of metal ions into the solution of crown-AuNPs, **B** Sensing response of crown-AuNPs towards various metal ions expressed in terms of change in fraction of absorption intensity (A_{600}/A_{527})



Aggregated crown-AuNPs can be redispersed by removing Cu^{2+} ions with EDTA; this is confirmed by the SPR absorption shift from 600 nm to 530 nm so that the SPR absorption is decreased (Fig. 6). After removing the supernatant using a centrifuge and suspending the residue in aqueous media, the dispersed crown-AuNPs can be reused to detect Cu^{2+} ions. Through this technique, the crown-AuNPs system can be used repeatedly for the detection of Cu^{2+} ions.

3.6 Interference Studies

In order to study the influence of the other metal ions on Cu^{2+} binding to crown-AuNPs, competitive experiments have been carried out in the presence of Cu^{2+} and other metal ions Al^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Ag^+ , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , and Zn^{2+} (Fig. 7). The SPR absorption shift caused by the mixture of

Fig. 4 Influence of pH on the absorbance ratio (A_{600}/A_{527}) of kryptofix21-AuNPs, **A**) absence of Cu^{2+} , **B**) presence of Cu^{2+} ($100 \mu\text{M}$)

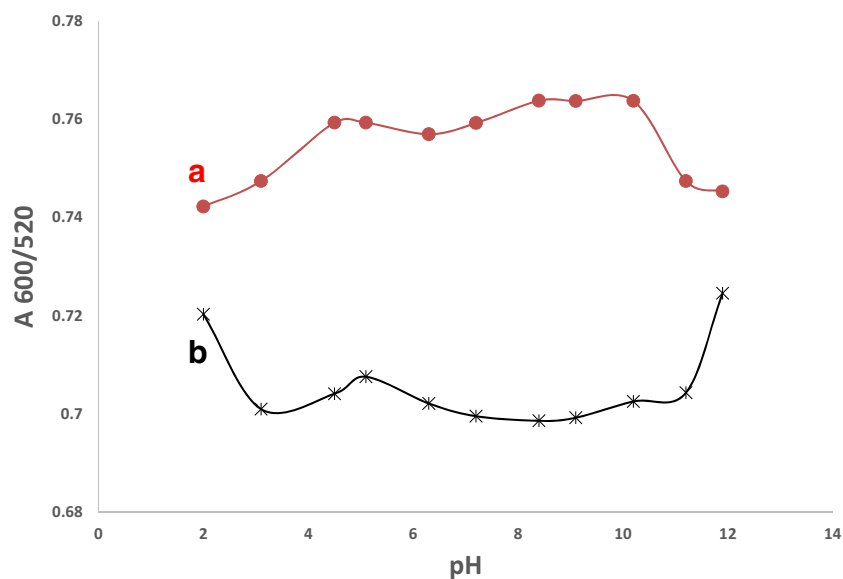


Fig. 5 Absorption spectral changes of crown-AuNPs in the presence of different concentrations of Cu^{2+} (10 – $250 \mu\text{M}$) in pH 7

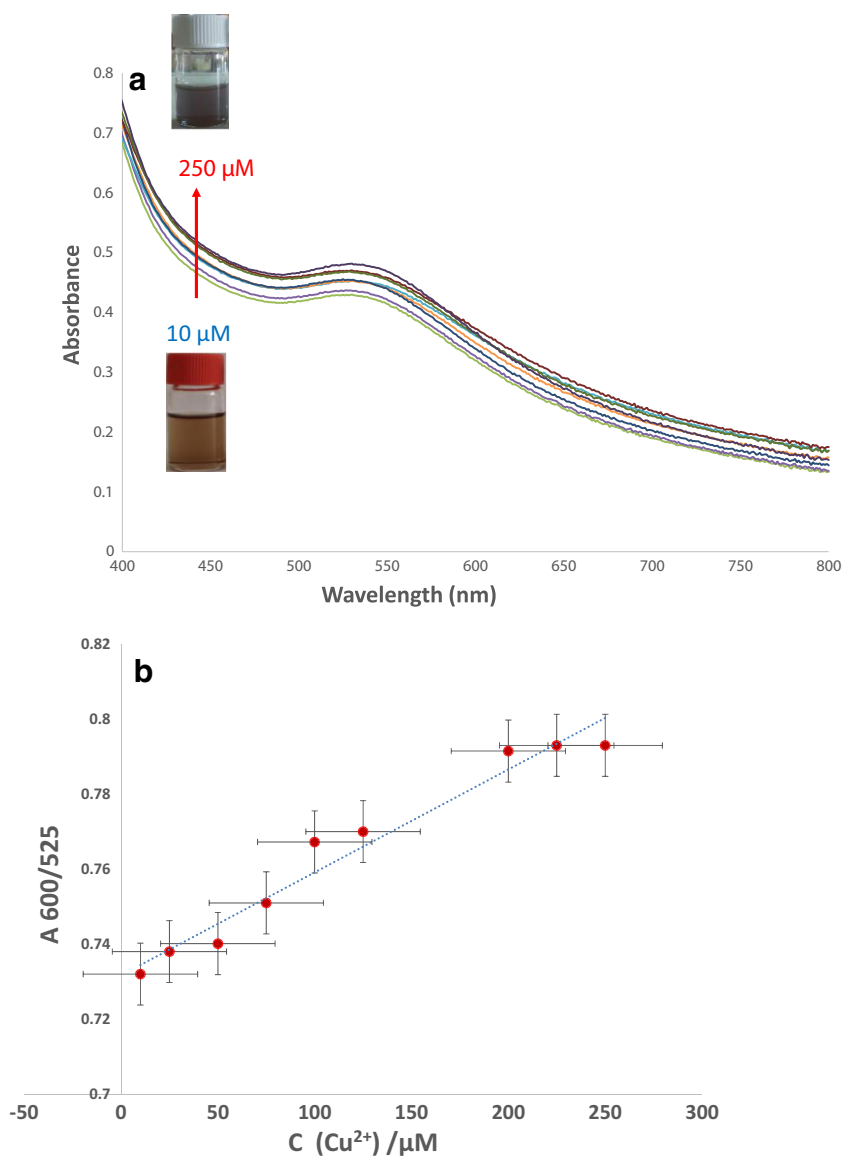


Fig. 6 Reversible binding of Cu^{2+} ($100 \mu\text{M}$) with crown-AuNPs in the presence of EDTA (10 mM)

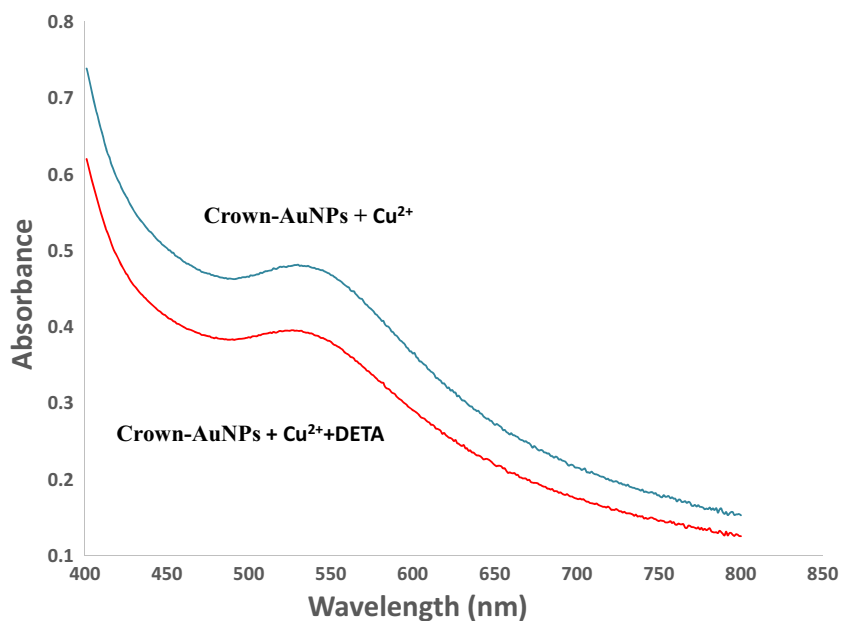


Fig. 7 Absorbance ratio (A_{600}/A_{527}) of crown-AuNPs in the presence of metal ions. Blue bars represent the addition of single metal ion ($100 \mu\text{M}$); Red bars represent the mixture of Cu^{2+} ($100 \mu\text{M}$) with another metal ion ($200 \mu\text{M}$)

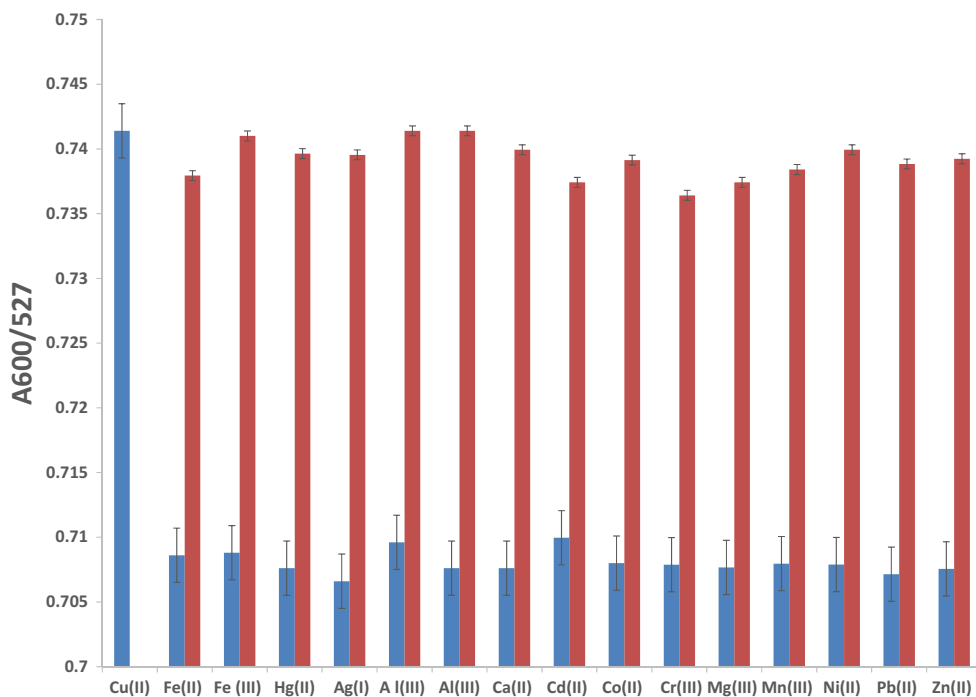


Table 1 A comparison of various colorimetric assays for Cu^{2+}

Entry	Probe	LODs	Real sample	Target	Refs
1	Protein-AuNPs	200 nM	Water solution	Hg^{2+} , Pb^{2+} and Cu^{2+}	[8]
2	Unmodified gold nanoparticles	10-0.1 μM	River water	Cu^{2+}	[9]
3	Pyridines-AuNPs	—	Water solution	Cu^{2+} and Ag^+	[10]
4	Crown-AuNPs	2.00 μM	Water solution	Cu^{2+}	this work

the Cu^{2+} with another metal ion is similar to that caused solely by Cu^{2+} . It indicates that the other metal ions do not interfere in the binding of crown-AuNPs with the Cu^{2+} . This result suggests that the Cu^{2+} is the only metal ion that can induce the aggregation of crown-AuNPs.

In addition, to show the advantages of the proposed sensor, a comparison table of the performances with different Cu^{2+} sensors is shown in Table 1. From Table 1, it can be seen that the detection limit of this proposed sensor (0.2 μM or 200 nM) is more acceptable than those of the other sensors [8–10].

4 Conclusion

In conclusion, the Cu^{2+} ion directed aggregation of gold nanoparticles (AuNPs) is observed through an interfacial complexation on 1,7-diaza-15-crown-5 gold nanoparticles (crown-AuNPs) surfaces. An interfacial crown-AuNPs/metal ion/Fu-AuNPs [2+1] sandwich complexation selectively occurs only with the Cu^{2+} on the surface of the AuNPs (Scheme 1). The color detection limit for the naked eye in this selective and sensitive method is 20 μM , and the lowest detection limit by the UV absorption measurement is approximately 0.2 μM (or 200 nM). To the best of our knowledge, this is the first example of a 1,7-diaza-15-crown-5 gold nanoparticle-based optical probe for the detection of the Cu^{2+} ion in aqueous solution. Finally, the method is compared with some existing methods for the determination of silver ions. The results are summarized in Table 1 indicating that the present work is simple, fast and cost-effective.

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