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Synthesis and Characterization of Eco-Friendly Gold Nanoclusters for Heavy Metal Ion Sensing

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Abstract

This research introduces a novel synthetic method for producing incredibly luminescent gold nanoclusters (AuNCs) using green tea extract (GTE). The synthesis process emphasizes sustainability and eco-friendliness by employing green tea extract as a reducing and stabilizing agent. The Cu(II) ions were traced using the synthesized GTE-AuNCs. Our recently devised method has enhanced the selectivity of AuNCs for Cu(II) ions. The green tea extract was incorporated into the synthesis process to increase and stabilize the quantity of AuNCs produced. Various instrumentation was employed to accurately differentiate the AuNCs based on their size, surface chemistry, and morphology. The fluorescence quenching of the AuNCs facilitated the GTE-AuNCs reaction with the target metal cations in the experiment. This sensing methodology offers a highly selective and accurate sensing method for Cu(II) in the 18.67 nM to 0.65 µM range, with a limit of detection (LOD) of 5.6 nM. Comparative research was conducted to determine the extent of selectivity of GTE-AuNCs for Cu(II) ions in comparison to other ions. AuNCs' substantial selectivity toward Cu(II) metal ions, despite the presence of interfering metal ions, subsequently facilitated the sensitive detection of Cu(II) metal ions in the environment. AuNCs are capable of detecting Cu(II) at levels that are acceptable within the nanomolar range. GTE-AuNCs were employed to detect Cu(II) ions in environmental samples, as determined by their properties.

Keywords: Nanoparticles; Gold; Green tea extraction; Cu(II); Water contamination; Heavy metals.

1. Introduction

Identifying heavy metal ions has emerged as a critical issue for environmental and analytical scientists because of their harmful impacts on the environment and human health. The human body's absorption of mercury and copper ions can result in significant repercussions, including genomic, neuronal, and immune system damage [1]. These metal ions are associated with several detrimental disorders, including Alzheimer's and Wilson's disease [2]. Conventional analytical techniques for detecting trace metal ions sometimes need costly equipment and intricate sample preparation processes. Consequently, advancing sensitive, practicable, reversible, and selective alternative methodologies is a highly focused research domain. Luminescence-based dyes or chromophores have emerged as attractive possibilities owing to their remarkable sensitivity, selectivity, and extensive dynamic ranges. These methodologies encompass both direct and ratiometric fluorescence intensity assessments [3-7].

Additionally, A wide range of fluorescent nanoparticles and biological molecules have been heavily utilized to develop sensitive chemical sensors that can detect a wide range of analytes, including metal ions, insecticides, gases, and biological molecules [8-12]. These sensors have the capability for quick, precise, and non-invasive assessment. Green synthesis, which eliminates the usage of harmful substances throughout the synthesis process, has garnered considerable interest owing to its economic efficiency, ecological sustainability, reduced energy use, and abbreviated processing duration. Furthermore, it obviates the necessity for detrimental stabilizers. Diverse natural substances, including plant extracts, microorganisms, and enzymes, can serve as sources for green synthesis. This work employed green tea extract (GTE) as a reducing and stabilizing agent in synthesizing gold nanoclusters (AuNCs). GTE is replete in phenolic chemicals, notably catechins, which have potent antioxidant and reducing capabilities [13,14]. These chemicals can efficiently reduce gold ions to generate AuNCs. The advancement of eco-friendly synthetic methods for AuNCs has attracted significant attention recently [15-19]. Various eco-friendly and uncomplicated techniques have been established to synthesize AuNCs that tend to dissolve in aqueous solutions. The synthesis pathways frequently employ diverse compounds as protective ligands and reducing agents, rendering these techniques particularly appealing for biological applications. Moreover, substantial advancements have been achieved in the synthesis methodologies of various kinds of AuNCs.

It is important to note that various mechanisms were proposed to elucidate the sensing mode. These mechanisms include internal charge transfer (ICT) [20,21], photo-induced electron transfer (PET) [22], which involves an acceptor or donor-excited state, and Forster resonance energy transfer (FRET) [23,24]. Additionally, ESIPT (excited state intramolecular proton transfer) probes absorb light radiation in the UV region and emit energy in the visible region.

AuNCs exhibit several advantageous characteristics, including as pronounced fluorescence, excellent water solubility, photostability, and biocompatibility. A pronounced Stokes shift between the excitation and emission peaks facilitates straightforward separation and characterization. Moreover, its stimulation using visible wavelengths mitigates auto-luminescence and hindrance from diverse biological objects in the surrounding medium, hence creating an interfering-free detecting media [25,26]. These attributes render AuNCs optimal candidates for developing non-toxic optical sensors for diverse

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biological applications. Various methodologies and protocols for regulated AuNCs synthesizing diverse scaffolds have been documented [27-29]. Recently, BSA-capped gold nanoclusters were produced by a one-pot, efficient, and environmentally friendly method in aqueous environments. The resultant AuNCs demonstrate steady emission throughout an extensive pH spectrum and have been utilized in diverse applications, including the sensing and imaging of numerous biomolecules [30-32]. Furthermore, many heavy metal ions, including Hg(II) and Cu(II), have been identified due to their propensity to associate with capped proteins, resulting in the dampening of AuNCs emission [33-36]. Significant biomolecules may be effectively identified by the fluorescence quenching "turn-off" methods of AuNCs [37,38]. In contrast, "turn-on" fluorescence techniques with a dark backdrop provide enhanced sensitivity and selectivity with minimal detection thresholds [39,40].

Molecular interaction analysis using green tea extract (GTE)-mediated gold nanoclusters (AuNCs) is superior to other approaches. Due to the biological features of green tea extract, GTE-AuNCs have remarkable selectivity for Cu(II) ions, unlike traditional methods that need extensive chemical modifications or additional reagents [41,42]. This streamlines and ensures accuracy. The AuNCs' fluorescence quenching process allows immediate, sensitive, non-invasive interaction monitoring with a low detection limit. This technology is ecologically friendlier and requires less equipment than spectroscopic or chromatographic procedures, making it suitable for laboratory and field use [43,44]. Its accuracy in detecting target molecules even with interfering species shows its durability and usefulness in complicated matrices.

Furthermore, the emission quenching of AuNCs by metal cations has been employed as a mechanism to regulate the luminescence of AuNCs chromophores for the selective luminescence activation detection of diverse analytes [45-48] is work involved the synthesis of new luminous AuNCs of diminutive size, utilizing green tea extract as a stabilizing and reducing agent. The resultant GTE-AuNCs were identified as functional sensors proficient in detecting distinct metal ions, Cu(II). The organic groups in green tea extract, such as amino, carboxyl, and hydroxyl groups of phenolic compounds, have a strong affinity for heavy metal ions, suppressing AuNCs luminescence. This interaction facilitates the quantitative identification of these essential metal ions. The established approach successfully detects Cu(II) in laboratory and ambient samples, with minimum interference from other ions. Consequently, GTE-AuNCs may be considered potential green fluorescence instruments for fast, selective, and sensitive Cu(II) detection in environmental and biological systems.

2. Experimental

2.1. Materials

The local market was the source of the practical material: green tea leaves. Sigma Aldrich Co. (www.Sigmaldrich.com) was the source of all compounds and reagents obtained at the highest purity possible. Spectrum Company procured a dialysis membrane with a 12000-14000 KD diameter. The organic solvents were of the highest quality available. The instrumentation part was inserted in the supporting information S2.1.

2.2. Preparation of the green Tea leaves extraction

Five grams of green tea leaves were finely pulverized and combined with 50 mL of bi-distilled water in a 100 mL volumetric vessel. The mixture was stirred at 100 °C for 2 hours. To isolate and acquire a pure extract, the resulting mixture went through filtering by employing filter paper. Furthermore, the resultant filtrate was centrifuged at 4000 rpm for a duration 20 minutes. The transparent solution was used as a reducing ingredient in the production of gold nanoclusters and was stored in the refrigerator at 4 °C. The extraction methodology was modified during the extract preparation process.

2.3. GTE-AuNCs production

The production of GTE-AuNCs was carried out in an aqueous medium, with certain modifications made by previous studies [49]. This technique will utilize green tea molecules to achieve the desired effects of stabilization and reduction. 5 mL of 10 mM HAuCl4 was added to 5 mL of GTE in a round flask with a capacity of 25 mL kept at 37 oC. After agitating the solution that was produced vigorously for three minutes, 0.3 mL of 1M NaOH was added simultaneously, and the combination was churned for an entire night. The solution proceeded through three distinct stages of color change, beginning with yellow, then moving to a light brown, and lastly arriving at a moderate brown. The resulting solution was dialyzed in water that was extremely clean, and the water that had been polluted was replaced every seven hours for a period of twenty-four hours to eliminate all contaminants. The quantum yield of the manufactured nanoclusters was evaluated by measuring the integrated emission intensity of the nanoclusters and the quinine sulfate probe in a sulfuric acid solution [50]. The reference wavelength for this measurement was 331 nm.

2.4. Trace process

Using an adequate quantity of 20 mM HEBES buffer with a pH of 7.4, we introduced the GTE-AuNCs solution by a factor of 20-fold dilution from the synthesized solution. Following that, we utilized the solutions produced in the succeeding measurements. The optical tests were then carried out with the excitation of 331 nm, with the GTE-AuNCs and 0.1 mM metal ion solutions that were being investigated being included in the preparation. To do more research on selectivity and sensitivity, various ions containing several metals were subjected to the similar rigorous evaluation circumstances.

3. Results and Discussions

3.1. GTE-AuNCs characteristics

A straightforward, distinct-step, green method utilizing commercially available green tea leaves extract (GTE) was developed to synthesize AuNCs at physiological temperature (37°C). GTE effectively synthesizes gold nanoclusters due to its polyphenol content, which acts as both a reducing and stabilizing agent. The polyphenols reduce gold ions to gold atoms, forming nanoclusters, then stabilizing these clusters by preventing aggregation. This eco-friendly and cost-effective method aligns with green chemistry principles. It has significant applications in biomedical fields, such as drug delivery, cancer treatment, and environmental applications. The simplicity and sustainability of using green tea extract make it a promising approach in nanotechnology. By adapting the pH value to approximately 12.5, we enhanced the reduction attendance of the

GTE constituents [51,52]. Additionally, using GTE as a capping agent improved the biocompatibility of the AuNCs. The GTE capping layer on the AuNCs facilitated surface modifications and the chelation of significant metal ions. Furthermore, GTE contains several essential elements that facilitate the creation of gold nanoclusters. The main constituents comprise polyphenols, including epicatechin, epicatechin gallate, epigallocatechin, and epigallocatechin gallate [53,54]. These polyphenols function as reducing agents, transforming gold ions Au3+ into gold atoms Au0, and as stabilizing agents, inhibiting the aggregation of the resultant nanoclusters. Moreover, green tea leaves encompass other bioactive constituents, such as alkaloids, caffeine, amino acids, and diverse volatile chemicals that enhance the overall stability and activity of the nanoclusters. The primary constituent of GTE plays a crucial role in mitigating the harmful effects of heavy metal cations due to its metal interaction capabilities.

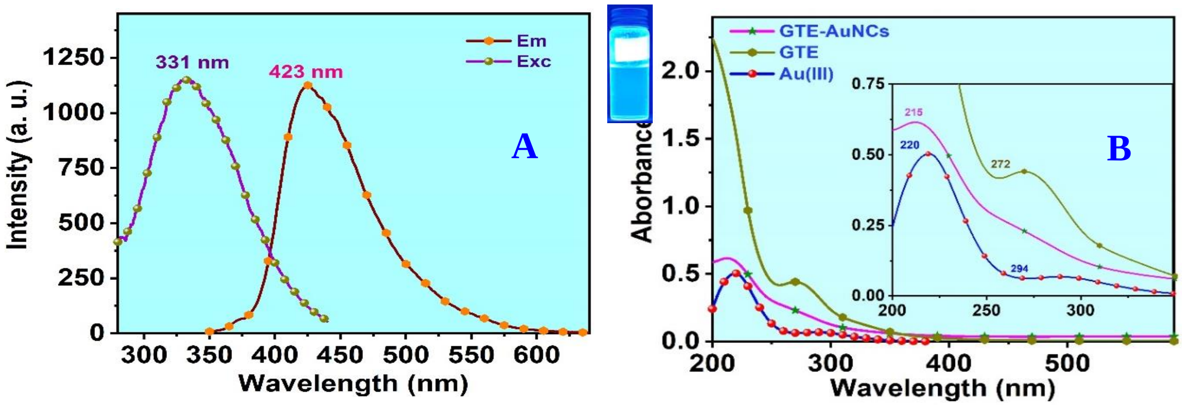

Fig. 1. (A) illustrates the GTE-AuNCs optical characteristics, and (B) the absorption of HAuCl4, GTE, and GTE-AuNCs.

The produced GTE-AuNCs solution has a pale brown color that is noticeable to the naked eye and displays a clear blue emission when exposed to UV light. The synthesized nanoclusters introduced Q_Y, a quantum yield of around 4.6% see Supporting information. The remarkable optical characters of *GTE*-AuNCs are validated by the fluorescence graph presented in Fig. 1A. Furthermore, the absorbance of $HAuCl_4$, *GTE*, and the synthesized AuNCs was documented (Fig. 1B). The fluorescence peak of GTE-AuNCs is located at 423 nm, with an excitation peak at 331 nm, as seen in Fig. 1A. The pronounced Stokes shift seen in GTE-AuNCs is ascribed to the novel use of GTE as a reducing agent. A sufficient Stokes shift inhibits self-quenching of the chemical probe ≈ 92 nm. Emission peaks may be identified in gold nanoclusters smaller than 5 nm. An absorption peak is seen between 200 and 550 nm, with a central wavelength of 218 nm for the *GTE*-AuNCs solution, as illustrated in Fig. 1B. The absorbance spectra of GTE-AuNCs markedly contrast with those of hydrogen tetrachloroaurate(III) and green tea extract, hence validating the development of nanoclusters. No absorbance peak at 520 nm, which indicates surface plasmon resonance (SPR) for bigger nanomaterials (>10 nm), is seen [55]. TEM imaging, DLS, and SD studies were performed to elucidate the nanoclusters' size and shape further. Figure 2A illustrates that the transmission electron microscopy (TEM) picture displays monodispersed, mostly spherical nanoclusters with an average size of 2 nm. The results indicate that the green *GTE* reduction process is an efficacious technique for producing high-performance gold nanoclusters. The DLS analysis and size distribution histogram (Fig. 2B and C) demonstrate that GTE-AuNCs are monodispersed and relatively. evenly distributed, with an average particle size of around 2 nm.

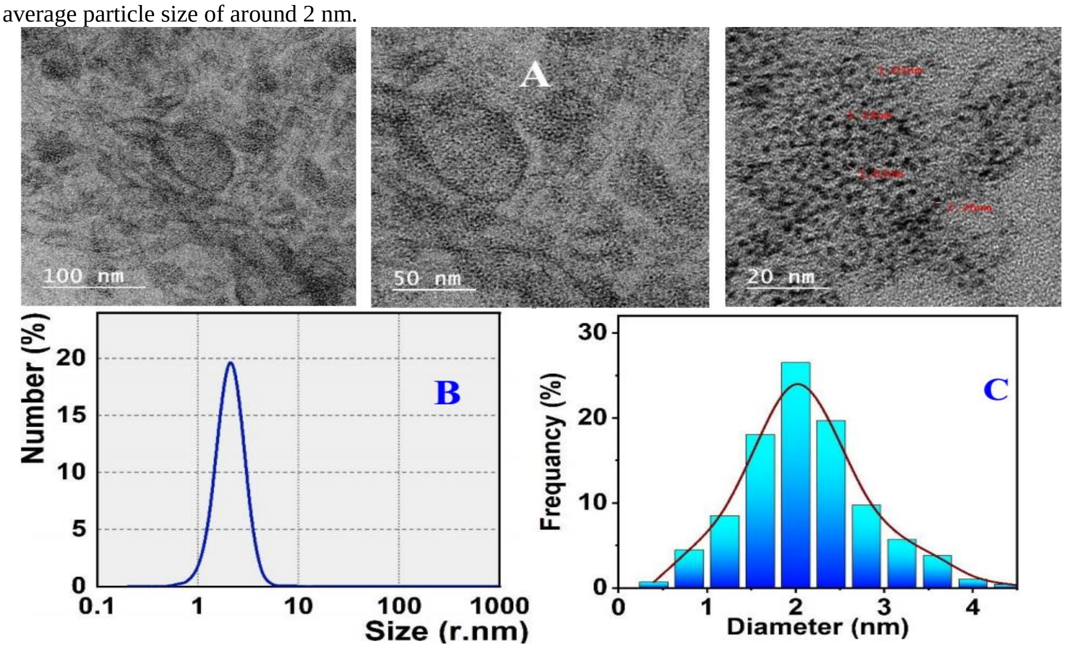

Fig. 2. (A) TEM images, (B) DLS, and (C) SD histogram of the GTE-AuNCs

X-ray photoelectron spectroscopy (XPS) was employed to conduct an additional investigation into the composition of *GTA*-AuNCs. As illustrated in Fig. 3A, the valence states of the gold atoms in *GTE*-AuNCs were investigated. In the XPS spectrum of gold, binding energy maxima are observed at 85.41 eV and 89.01 eV, corresponding to $4f_{7/2}$ and $4f_{5/2}$, respectively. This analysis verifies the presence of Au0 and Au+1 species in GTE-AuNCs. It is intriguing that the binding energy exhibits a blue shift compared to previous research on AuNCs, implying that Au^0 plays a substantial role in the constitution. The binding energy's significant impact is indicated by its proximity to Au0, which contributes to the brilliant fluorescence of *GTE*-AuNCs. The nanoclusters demonstrate robust fluorescence, even though Au^{+1} is minimal in the synthesis process. Additionally, the XPS survey (Fig. 3B) identifies the presence of carbon, nitrogen, and oxygen, which is consistent with the capping agent of green tea extract. This demonstrates that the GTE ligand efficiently safeguarded the synthesized AuNCs' surfaces.

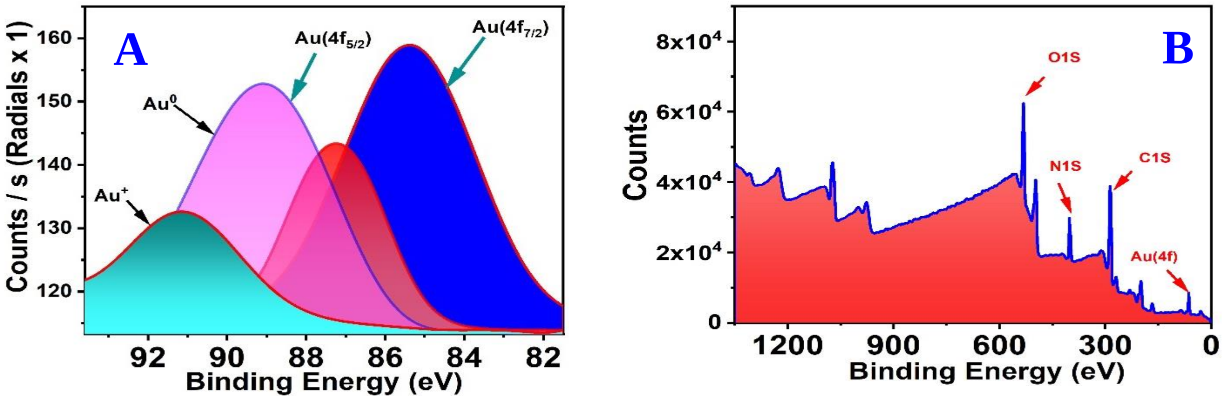

Fig. 3. (A) The high-resolution XPS spectra of Au 4f7/ 2; and (B) Survey spectra of GTE-AuNCs.

3.2. FT-IR Measuring

The FTIR spectra depicted in Fig. 4 compare two samples, *GTE*, represented by the red line, and *GTE*-AuNCs, represented by the blue line. This analysis emphasizes the unique functional groups present in each sample, offering a deeper understanding of their chemical composition and interactions. The O-H stretch of H-bonded hydroxyl groups, abundant in constituents such as alcohols and phenols, is represented by the peak at 3316 cm^{-1} in the FTIR spectrum of the *GTE* [56]. This peak suggests the presence of these functional groups in the green tea extract. The peak at 2949 cm^{-1} is associated with carboxylic acids and alkenes, which implies that these compounds are also present in the green tea extract. This peak demonstrates the diverse nature of the compounds in green tea. The presence of flavonoids and polyphenols, significant components of green tea, is responsible for the peak observed at 1633 cm^{-1}. This peak indicates the C=C stretch in aromatic rings, a distinguishing characteristic of these compounds. The presence of aromatic compounds in the green tea extract is further confirmed by the peak at 1451 cm^{-1}, which is attributed to the C-C stretch in aromatic rings. Furthermore, the peak at 1245 cm^{-1} is linked to the C-N stretch in aliphatic amines, suggesting the presence of these functional groups in the green tea extract. The C-O stretch in alcohols and esters is represented by the final significant peak at 1100 cm^{-1}, which implies that these compounds are also present in the green tea extract. Similar peaks are observed in the FTIR spectrum of the AuNCs synthesized using green tea extract (*GTE*-AuNCs), but there are significant differences in intensity and position [57]. The peak at 3316 cm^{-1} is still present, suggesting that hydrogen-bonded hydroxyl groups are a critical component of the gold nanoclusters. The presence of the peak at 2949 cm^{-1}, which is associated with carboxylic acids and alkenes, indicates that these functional groups are still present in the gold nanoclusters. The peak at 1633 cm^{-1}, corresponding to flavonoids and polyphenols, is still visible, suggesting that these compounds remain a substantial component of the gold nanoclusters. The gold nanoclusters also exhibit peaks at 1451 cm^{-1}, 1245 cm^{-1}, and 1100 cm^{-1}, which are associated with aromatic compounds, aliphatic amines, and alcohols/esters, respectively [58]. The FTIR spectra of the gold nanoclusters and the green tea extract indicate that the functional groups present in the green tea extract are retained in the gold nanoclusters, albeit with some modifications. These modifications may result from the interaction between the gold nanoclusters and the green tea extract, which could alter the intensity and position of the peaks. This interaction is significant because it offers a glimpse into the chemical composition and interactions of the green tea extract and the gold nanoclusters, which could have implications for their potential applications in various disciplines, including nanotechnology and medicine.

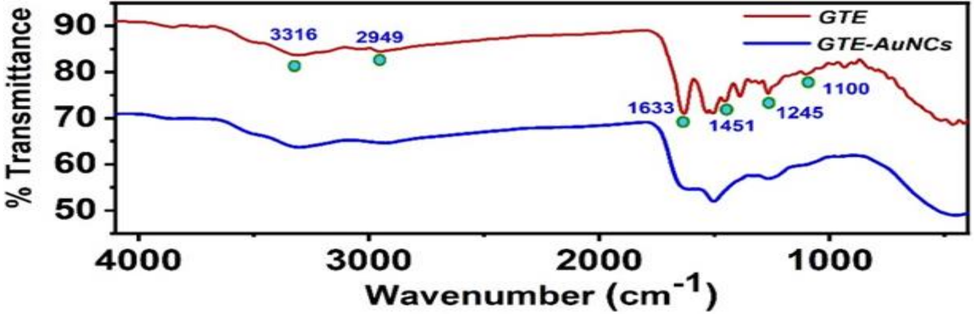

Fig. 4. IR spectra of GTE and GTE-AuNCs

3.3. Optimum conditions of the synthesis process

We investigated how the reaction temperature changed the luminescence efficiency of the *GTE*-AuNCs that had already been made. The luminescence gets brighter when the mixture temperature goes from 22 °C to 37 °C. When the temperature is raised to 50, 60, or 70 ˚C, the emission levels drop by a large amount. The behavior we see can be elucidated by the reality that bigger nanoclusters form at high temperatures, which makes the fluorescence of AuNCs agglomerated [59]. Because of this, the best temperature is found to be 37 ˚C, as shown in Fig. 5A. It has been noticed that the levels of fluorescence in *GTE*-AuNCs rely on how much *GTE* is present. It's interesting to note that the light intensity of *GTE*-AuNCs increases disproportionately when 5 mL of *GTE* is added to a mixture of 2 to 7 mL of *GTE* (Fig. 5B). When the *GTE* concentration goes up to 7 mL, the light level of *GTE*-AuNCs goes down, which is not what we want to happen. As a result, 5 mL of *GTE* is the best quantity, as shown in the inset of Fig. 5B.

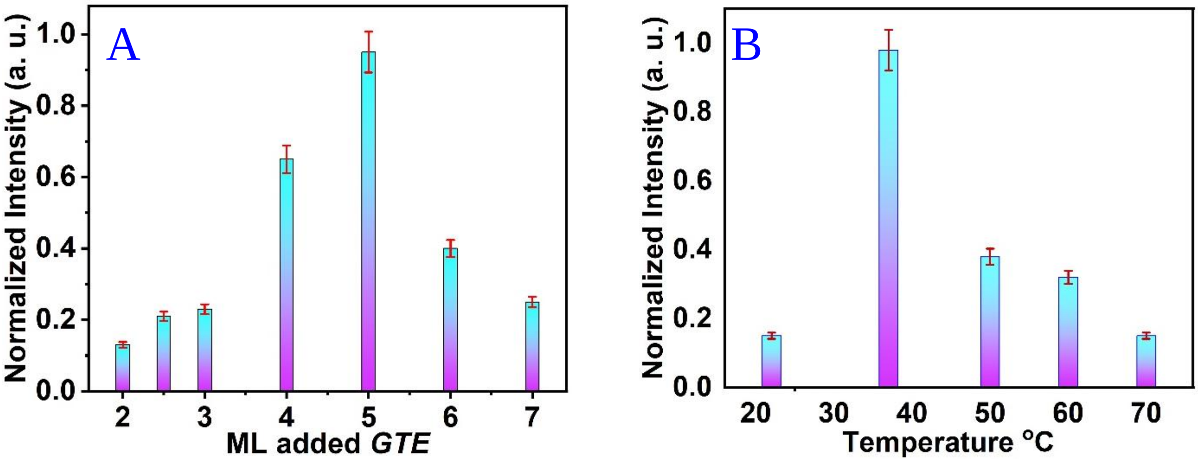

Fig. 5. (A) Influence of the initial [GTE] and (B) Influence of temperature on the manufacturing of GTE-AuNCs.

3.4. GTE-AuNCs selectivity

We initially assessed the fluorescence of GTE-AuNCs in the attendance of Cu(II) and various additional metal cations, encompassing alkali, alkaline earth, and transition metal ions. The GTE-AuNCs demonstrated a significant response to mercury ions, with approximately 89.6% of the fluorescence signal suppressed by 6.5 µM Cu(II). Additionally, the other metal ions did not produce noteworthy quenching at the concentration of 6.5 µM, as shown in Fig. 6. The fluorescence quenching of GTE-AuNCs by Cu(II) delivers an efficient method for their tracing. The detection limit for Cu(II) is 14.5 nM, situated within the nanomolar range. Therefore, additional handling is obligatory to distinguish the quenching phenomena.

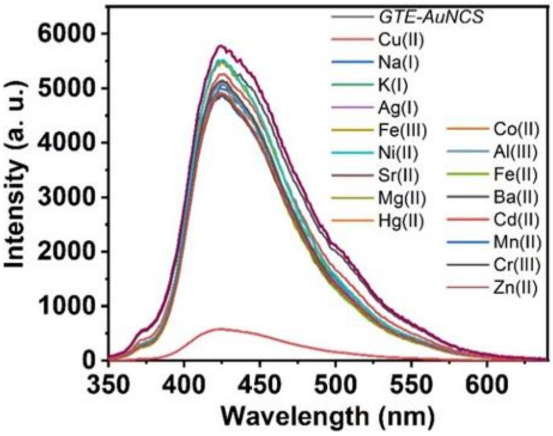

Fig. 6.The influence of different cations on the *GTE*-AuNCs luminescence.

3.5. Sensing Mechanism

In this context, the process is predicated on the notion that Cu(II) is chelated with the surface of the *GTE*-AuNCs by promoting the formation of a metal-complex with the active functional groups of the *GTE* of the *GTE*-AuNCs. This resulted in a significant reduction in the fluorescence of the *GTE*-AuNCs, most likely by an electron transfer mechanism. The extreme blue fluorescence of *GTE*-AuNCs, which can be quenched clearly, is displayed in Fig. 7A due to the titrimetric reaction of *GTE*-AuNCs in the occurrence of Cu(II) solution. A diminishment in the fluorescence of the *GTE*-AuNCs is observed due to the addition of Cu(II) ions, as shown by the subsequent emission spectra; nevertheless, the wavelength of the highest peak of the AuNCs is not affected by this addition. Additionally, there is no overlap between the fluorescence of *GTE*-AuNCs and the absorption of Cu(II) ions within the spectrum. That being the case, resonance energy transfer cannot be established as the mechanism that has been postulated [60]. AuNCs that were stabilized with various scaffold molecules were reported by several distinct sorts of research study outcomes. Based on the aggregation of nanoclusters, these nanoclusters were employed to detect substantial metal ions [61]. This phenomenon is brought about by creating a metal-complex between the molecules of the surface scaffold and the metal ions that are now in activity.

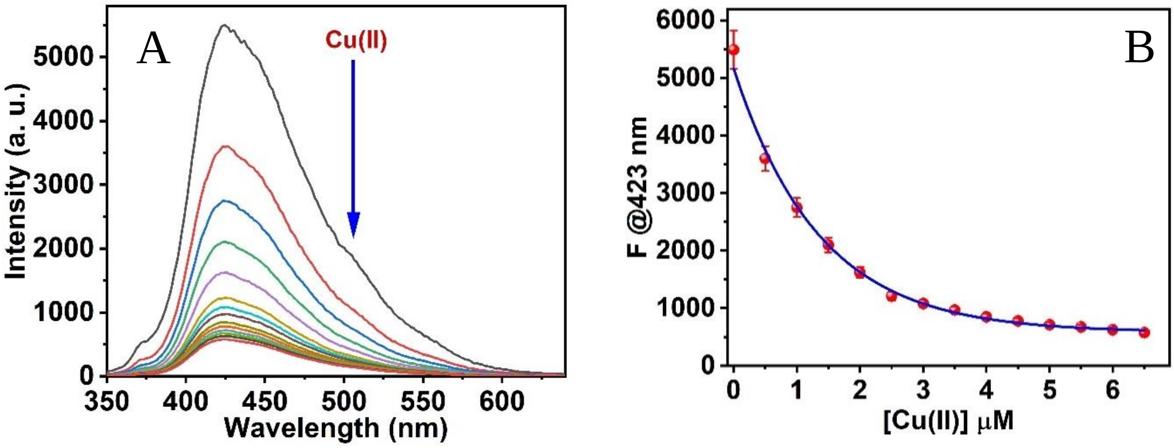

Fig. 7: (A) The optical titrimetric reaction involves GTE-AuNCs and Cu(II) ions; (B) Relation of GTE-AuNCs fluorescence intensity versus [Cu(II)].

The quenching phenomenon of *GTE*-AuNCs in the presence of copper ions is accredited to the spontaneous Cu(II)/Au$^+$ reaction within the structure of the nanoclusters. A *GTE*-AuNCs solution was introduced in this experiment in 20 mM HEBES buffer at pH 7.4 with Cu(II). The results were conducted in Fig. 7A. the *GTE*-AuNCs fluorescence decreases with the increasing concentration of Cu(II) ions. The fluorescence intensity stabilizes at 0.65 µM. Fig.7B illustrates the correlation between the fluorescence intensities of *GTE*-AuNCs and varying concentrations of metal ions. This demonstrates that the sensing mechanism for Cu(II) ions, in the presence of the sensor nanoclusters, operates through a quenching mechanism within the concentration range of 0 to 0.65 µM.

The Stern-Volmer equation was employed [62], and a graph including (F_0/F) against [Cu(II)] was generated, as shown in Fig. 8. A linear association was found throughout a concentration range of 0-14 µM, providing a correlation value (R^2) of 0.993. The limit of detection (LOD) was calculated to be 5.6 nM, based on the premise that optical emissions could be determined with an accuracy of ±1% [63]. This LOD is much lower than the Cu(II) value (31.5 µM) indicated by the WHO for drinking water quality guidelines [64]. Thus, the optical sensor GTE-AuNCs considerably impacts the detection of Cu(II).

$$\mathbf{F_0/F = 1 + K_{sv}\,[Q]}$$

Where F_0 and F are emissions of *GTE*-AuNCs and *GTE*-AuNCs in the occurrence of Cu(II) metal ions, K_{sv} is the Stern Volmer constant, and [Q] is the quencher molarity based copper ions.

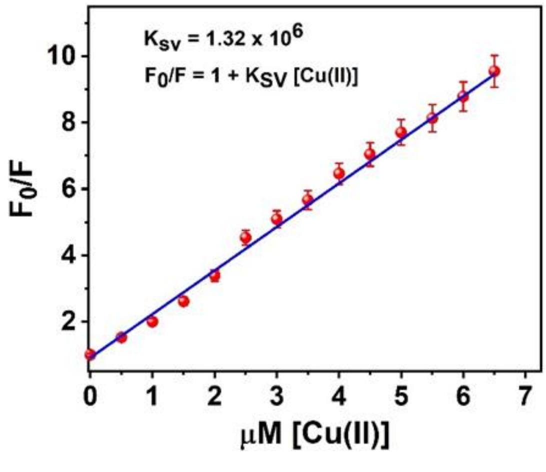

Fig. 8. Stern Volmer equation for the GTE-AuNCs versus different [Cu(II)].

3.6. Affinity interaction

The fluorescence spectra variations of the *GTE*-AuNCs probe were studied in the presence of various Cu(II) concentrations to estimate the binding constant. This was done to understand the mechanism of metal-nanocluster binding better. A modified version of the Stern-Volmer equation was utilized to locate the binding constant.

$$F_0/F_0\text{-}F = 1/A + 1/A.\ K_b\ [Q]$$

In the equation shown here, the symbol F_0 represents the fluorescence intensity of the unbound ligand AuNCs, the symbol F represents the fluorescence intensity of the Cu(II)-AuNCs complex, the symbol Q represents the concentration of [Cu(II)], and the symbol A represents a constant. The symbol K_b represents the binding constant [65,66]. A linear connection was seen when $F_0/(F_0/F)$ was graphed against the concentration of 1/[Q]: ($y = \alpha + \beta x$), where $y = F_0/(F_0 - F)$, the intercept equals 1/A, the slope equals $1/A.K_b$, x equals 1/[Q], and K_b was derived from α/β (Fig. 9). Inferred from the fluorescence titration curves of the AuNCs probe with Cu(II), K_b, the binding association constant, was determined to be 3.38×10^6 M^{-1}.

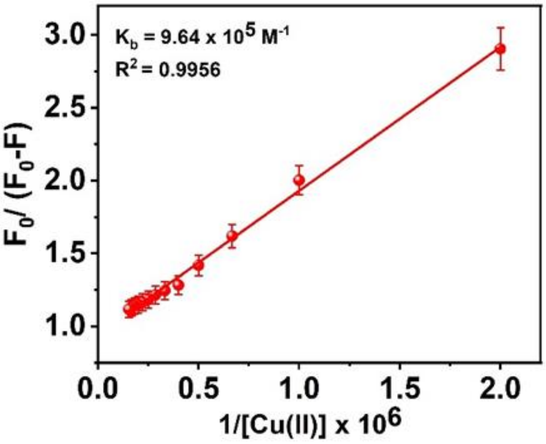

Fig. 9. Modified Stern-Volmer relation for the *GTE*-AuNCs system.

3.7. GTE-AuNCs Selectivity

To evaluate the *GTE*-AuNCs selectivity, we investigated the impact of a variety of cations at a concentration of 0.65 µM on GTE-AuNCs under optimal settings as shown in Fig. 10A. The fluorescence intensities of the Cu(II)-*GTE*-AuNCs system remained unaffected in the presence of other cations, suggesting that *GTE*-AuNCs could sense Cu(II) ions selectively. Furthermore, it has been demonstrated that the luminescence intensity of AuNCs can be reduced by copper ions by transferring electrons/energy. The quenching effect of Cu(II) is ascribed to the ingredients of *GTE*, which chelate Cu(II) ions and induce fluorescence quenching. Additionally, flavonoids, carboxylic acids, and polyphenols are biologically active compounds and substantial components of green tea [67]. The luminescence of the AuNCs in the Cu(II)-*GTE*-AuNCs system is significantly improved by adding EDTA solution. This enhancement results from the Cu(II) ions binding to EDTA, which effectively removes Cu(II) ions from the *GTE*-AuNCs surface and restores the luminescence intensity of the AuNCs. The fluorescence of AuNCs recovered to approximately 89.8% of its initial value in the presence of EDTA solution after five cycles, as illustrated in Fig. 10B. This is a remarkable recovery. The luminescence intensity of *GTE*-AuNCs remained consistent with subsequent cycles, remaining unchanged after five cycles. Furthermore, the highly selective detection of Cu(II) ions is facilitated by the kinetic differences in the restoration of AuNCs luminescence. Consequently, the *GTE*-AuNCs technique exhibited sufficient reproducibility for determining Cu(II) ions over a five-cycle.

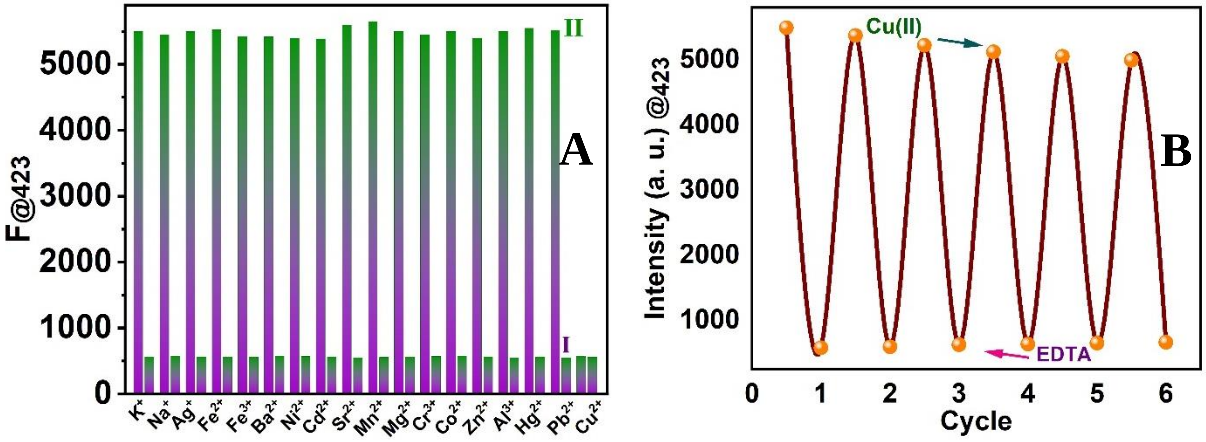

Fig. 10. (A) The emission of GTE-AuNCs (II) in the accreditation of several cations and (I) in the presence of Cu(II) ions and the other cations; and (B) The addition of EDTA returns the GTE-AuNCs emission.

3.8. Detection of metal ions in real samples

This study focused on detecting Cu(II) metal ions in mineral and tap water samples with a *GTE*-AuNCs sensor film. The analyzed water samples were employed directly without further processing. The detection was performed following the adjustment of the samples in a 20 mM HEPES buffer solution at pH 7.4. Additionally, specific Cu(II) concentrations were individually introduced to the real samples. The obtained findings are contingent upon the standard curve derived from the experimental series. The amounts of Cu(II) in mineral and tap water samples have been discovered. The findings presented in Table 1 indicate that the average recovery range for Cu(II) detection was 97.0% to 98.66%. The obtained results were evaluated compared to the ICP-MS data, indicating that this method is crucial for detecting Cu(II) in environmental samples. The sensing method demonstrated reasonable specificity and sensitivity in detecting Cu(II) ions, but its real-world applications confront hurdles and constraints. Environmental monitoring, where selective detection of Cu(II) ions among various ions is beneficial, is one such application. The availability of green tea extract of consistent quality and quantity for large-scale AuNC manufacturing may affect scalability. GTE-AuNCs' long-term stability under pH variations and interfering chemicals must also be assessed. Further research should examine this method's adaptation to complicated matrices and its inclusion with automated sensing systems to promote real-world use. These factors stress the need to optimize the mechanism for practical relevance while retaining its green synthesis and environmental friendliness.

Table 1. Applying the chemical sensor in real water samples using *GTE*-AuNCs (n-3).

Samples	Added Cu(II) µM	ICP-MS µM	Found µM	RSD (%)	Recovery (%)
Mineral water	0.10	0.101	0.097	1.08	97.00
	0.30	0.303	0.296	0.91	98.66
	0.60	0.605	0.589	0.82	98.16
Tap water	0.10	0.102	0.098	1.11	98.00
	0.30	0.306	0.293	0.86	97.66
	0.60	0.606	0.591	0.84	98.50

4. Conclusion

This study illustrates the efficient synthesis of gold nanoclusters (AuNCs) with green tea extract (GTE) through an environmentally friendly, one-pot, and straightforward method. GTE has been employed for the first time as a novel reducing and capping agent in synthesizing AuNCs. Our research introduces a novel sensing methodology enabling AuNCs to function as eco-friendly optical sensors. This method uses the fluorescence intensity of AuNCs to detect copper cations. The robust chelation ability of green tea constituents on AuNCs concerning Cu(II) resulted in considerable fluorescence attenuation, facilitating the quantitative evaluation of Cu(II) levels. Moreover, the fluorescence-quenching effect is markedly enhanced by the reduction of Cu(II) on the surface of AuNCs in the presence of Au^+, providing an effective method for Cu(II) detection. Our experiment also evaluated the impact of various metal ions on Cu(II) detection. The results indicate that GTE-AuNCs exhibit considerable selectivity and sensitivity for Cu(II) in the presence of other metal ions, hence minimizing potential interference and ensuring accurate detection. This innovative technology underscores the potential of green chemistry and provides a sustainable, eco-friendly approach for enhancing sensing devices. The pronounced fluorescence-quenching properties and significant chelation ability of GTE-AuNCs make them an effective tool for analyzing actual samples, particularly in the detection of Cu(II) in environmental specimens. Our discovery represents substantial advancement in the development of eco-friendly, efficient, and highly selective sensors for the detection of hazardous metal ions, especially copper.

5. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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