Green Chemical Synthesis of N-Cholyl-L-Cysteine Encapsulated Gold Nanoclusters for Fluorometric Detection of Mercury Ions

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Abstract
Herein we report a simple, single-step, cost-effective, environmentally friendly, and biocompatible approach using sodium salt of N-cholyl-L-cysteine (NaCysC) capped gold nanoclusters (AuNCs) with green emission properties at above the CMC in aqueous medium under UV-light irradiation. The primary and secondary CMC of NaCysC was found to be 4.6 and 10.7 mM respectively using pyrene as fluorescent probe. The synthesized AuNCs exhibit strong emission maxima at 520 nm upon excitation at 375 nm with a large Stokes shift of 145 nm. The surface functionality and morphology of NCs are studied by fourier transform infrared spectroscopy, dynamic light scattering studies and transmission electron microscopy. The forma-
tion of AuNCs was completed within 5 h and exhibit high stability for more than 6 months. The NaCysC templated AuNCs selectively quenches the Hg2+ ions with higher sensitivity in aqueous solution over the other metal ions. The fluorescence analysis of Hg2+ showed a wide linear range from 15 to 120 µM and a detection limit was found to be 15 nM.

Keywords Fluorometric detection · Sodium salt of N-cholyl-L-cysteine · Mercury ions · Green emitting gold nanoclusters

Introduction
In the ever-expanding field of nanomaterial research, noble metal nanoclusters (MNCs) in particular silver (Ag), gold (Au) and copper (Cu) have been emerged as a new class of luminescent materials and attracted great attention in the area of chemistry, physics, materials science, and biomedical sciences [1, 2]. These MNCs possess size close to the Fermi wavelength of conduction electrons and show discrete energy level as compare to large metal nanoparticles (MNPs) [3]. Besides, in this size regime they exhibit intriguing molecule-like properties such unusual intrinsic magnetism, step like absorption feature and exhibit size-dependent tune-
able emission properties from visible to NIR region [4, 5]. Among the various molecular like properties, luminescence is an significant properties of MNCs and utilized field of imaging, detection, drug delivery and nanotherapy [6–8]. In view of above mentioned applications, AuNCs have been focused as most widely studied luminescent materials by many research groups during the last two decades owing to their easy to synthesis, low toxicity, good water solubility, ultra-small size as compared to semiconductor QDs and excellent photostability, large Stokes shift and brightness than traditionally used organic dyes [9–11]. Thus, AuNCs can be used as potential fluorescent probe for biological and chemical sensing, bioimaging, drug delivery, small biological molecule detection [6–10] and antibacterial agents [3, 12, 13].

However, due to their ultrasmall size AuNCs has tendency to form aggregates when the capping molecules are not efficient [12]. Therefore, selection of capping molecules plays a significant role in the formation of AuNCs, which can prevent the super atoms from aggregation and keep the size dependent fluorescence property from ultraviolet (UV) to near infrared (NIR) by controlling the core size of AuNCs [14]. Up to now, variety of protocols have been developed to synthesize AuNCs using different kinds of ligands or capping molecules such as polymers [15], surfactants [16], DNA [17], amino acids [18], organic thiolate molecules [19] and dendrimers [20] with different core sizes, chemical
compositions, surface ligands and emission properties. Water soluble, monodisperse, blue light emitting Au₈ nano dots was reported using biocompatible poly(aminodiamine) (PAMAM) dendrimers as hosts [21]. Qu et al. elaborated about various synthetic strategies on fluorescent AuNCs and recent advances in biological applications [22]. In recent years, AuNCs were extensively used as probe for sensing of toxic metal ions owing to their size dependent luminescence properties, high sensitivity towards analytes, excellent water solubility and photo-stability [23].

Regarding the heavy metals, they are highly poisonous even at trace levels, endangering to human health through the air, beverages, and the food chain, wherein water plays a key role [24, 25]. Among the various heavy metals, mercury ion (Hg²⁺) is of great concern since they exhibit high toxicity to humans and aquatic species even at low concentrations and bioaccumulation of Hg²⁺ ions can cause serious health problems [26]. Solvated mercuric ion (Hg²⁺) is one of the most stable inorganic forms, which can damage the brain, heart, kidney, stomach, and intestines, even at very low concentrations [27]. Owing to their advantage of strong affinity of metallophilic Au⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ético

Experimental Section
Materials and Methods

Materials

L-cysteine and hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) were purchased from LOBA chemi, India. Salts of the different ions such as Na⁺, K⁺, Ca²⁺, Li⁺, Cd²⁺, Hg²⁺, Fe²⁺, Co²⁺, Cr³⁺, Cu²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ were procured from SRL chemicals Pvt. Ltd., India. All heavy metal salt solutions (1 × 10⁻⁵ M) used for the experiments were prepared by mixing the required amount of salt in double distilled water and pH of the solution was adjusted by adding either 1 N of HCl or NaOH. All glassware were thoroughly cleaned with aqua-regia (HCl: HNO₃ = 3:1 (v/v)) and rinsed well with triple distilled water prior to use.

Synthesis of Sodium Salt of N-Cholyl-L-Cysteine

Sodium salt of N-cholyl-L-cysteine (NaCysC) was prepared by adopting our previous protocol with slight modifications [36]. Briefly, a magnetically stirred solution of 1.0 mM of L-cysteine methyl ester hydrochloride was added into the 0.5 mM cholic acid in dry DMF (2 mL). Then DEPC (0.6 mM) and Et₃N (0.8 mL) were added into the reaction mixture and the resulting suspension was stirred at RT for 2 h as shown in Scheme 1. After the completion of reaction, the product was extracted with EtOAc and the combined extracts were washed with double distilled water and evaporated to dryness. The residue was then refluxed for 30 min in 10 mL of 5% methanolic NaOH. The solvent was evaporated under reduced pressure and the hydrolyzed product was dissolved in 10 mL of water and acidified with 5% H₂SO₄ with constant stirring. The precipitated solid was filtered, washed with water and dried to give the crude amino acid conjugate of 75% yield, which was then recrystallized from an appropriate solvent.

Experimental Section

Materials and Methods

Instruments

UV–visible spectroscopy measurements were carried out on Techcomp UV-2301II spectrophotometer operated at a resolution of 1 nm. High-resolution transmission electron microscopic (HR-TEM) images were recorded with a JEOL JEM 2100 equipped with a Gatan imaging filter. The HR-TEM analysis was conducted by placing a drop of the NCs solution on carbon-coated copper grid and followed by solvent evaporation under vacuum as per manual instructions. Dynamic light scattering (DLS) measurement was recorded for NCs solutions using Nanotrac Ultra NPA 253 from Microtrac, U.S.A. The emission spectra of pyrene was measured by Fluoromax 4 (Horiba Jobin Yvon) spectrofluorimeter equipped with 150 W Xenon lamp. The spectra was monitored from 350 to 500 nm at a scan rate of 30 nm/sec upon exciting the pyrene molecules at 340 nm. The slit widths of excitation and emission were 20 and 1.5 nm, respectively. Band pass filter (10BPF10-340) was used to avoid white light from the monochromators. For FT-IR analysis the pressed pellet was prepared by grinding lyophilized NaCysC capped AuNCs powder with KBr in a 1:100 ratio and analyzed in the spectral range of 4000–500 cm⁻¹.
Sample Preparation

Stock solution of pyrene (3 × 10⁻⁵ M) was freshly prepared by gentle evaporation of appropriate amount pyrene solubilized methanol solution, followed by addition of an accurate volume of double distilled water in a volumetric flask and sonicated for 30 min. The synthesized NaCysC was hygroscopic and lyophilized salts were used to prepare known concentration of stock solutions. The stock solutions of 16.0 mM of NaCysC was prepared using double distilled water and the actual pH of the solutions were found to be 6.5. Since NaCysC was soluble only in neutral and basic pH, NaOH was used to adjust the pH of the solution. Subsequent dilutions were made from this stock solution to obtain the desired final concentration. Aliquots of 300 μL stock solutions of pyrene were added to 4 mL of NaCysC to obtain a final concentration of 2.25 × 10⁻⁶ M of pyrene to measure the CMC. The solutions were kept for few hours for the encapsulation of pyrene molecules.

Synthesis of NaCysC Stabilized AuNCs

The NaCysC stabilized AuNCs was prepared by mixing aqueous solution of 0.1 mL of HAuCl₄ (10 mM) with 2 mL of NaCysC (above the CMC) in 5 mL disposable glass vial containing 2.4 mL of double distilled water. The reaction mixture was stirred vigorously for 2 min, followed by the addition of a certain amount of 1 M NaOH to adjust the reaction pH to 9.0. Thereafter, the resulting solution was kept under UV-light irradiation at 365 nm for 5 h and the formation of NCs was monitored by UV–visible and fluorescence spectroscopy.

Fluorometric Detection of Heavy Metal Ions

Under optimized concentration the synthesized AuNCs was used as fluorescent probe owing to their size dependent emission properties and tendency to quenches the emission in the presence of analytes. Hence, the following metal ions were used to evaluate the selectivity of AuNCs: Na⁺, K⁺, Ca²⁺, Li⁺, Cd²⁺, Hg²⁺, Fe²⁺, Co²⁺, Cr³⁺, Cu²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ at a fixed concentration of 70 μM. The changes in the emission intensity of solution was monitored by fluorescence spectroscopy.

Result and Discussion

Determination of CMC of NaCysC

Critical micellar concentration (CMC) is a crucial parameter for surfactants for wide applications.

The CMC values of surfactants not only correlate to their molecular structures and also sensitive to the polarity of the microenvironment. Bile acids are physiological surfactants which contains fused aliphatic tetracyclic rings with chemically non-equivalent hydroxyl groups and easily modifiable carboxylic group [37]. Owing to the above features, bile acids are exhibit primary and secondary CMC through hydrophobic and hydrogen bonding interactions [38]. Therefore, CMC for NaCysC was determined by measuring the intensity ratio of third and first (I₃/I₁) highest vibronic bands of pyrene in the emission spectra that are sensitive to the polarity of microenvironment. A very low concentration of pyrene (2 × 10⁻⁶ M) was used in this study, hence only negligible effect on the micellization process was noticed. The changes in the I₃/I₁ ratio of pyrene at a fixed concentration with increased concentration of NaCysC showed a sigmoid variation (Fig. 1). The point of intersection of the horizontal line and the
line of inflation represents formation of both primary and secondary CMC of NaCysC and are found to be 4.6 and 10.7 mM respectively. The significant decrease in the CMC of NaCysC solubilized pyrene as compare to pure sodium cholate (NaC) could be due to the increase in the hydrophobicity that favours the formation of CMC at a lower concentration.

**Optical Properties of AuNCs**

The formation fluorescent AuNCs was confirmed by demonstrating the reaction between HAuCl₄ (1 × 10⁻⁶ M) and NaCysC in below and above the CMC in basic pH 9.0 under UV light irradiation at 365 nm (Fig. 2). In below the CMC, step like feature was observed in the UV region in addition to week surface plasmon resonance (SPR) between 500 to 600 nm could be due to the formation of mixture of both AuNCs and AuNPs (curve a). However, at above the CMC no SPR peak was observed in the visible region which indicates that NaCysC favours only AuNCs formation rather than NPs (curve b). Further the synthesized AuNCs exhibit a green emission properties when the solution was kept under UV light at 365 nm. Hence, above the first CMC of NaCysC (5.8 mM) was chosen as the optimum concentration for the preparation of AuNCs. The NaCysC stabilized AuNCs exhibits a strong emission peak at 520 nm with a full width at half maximum (FWHM) of 95 nm, when excited at 370 nm (inset of Fig. 2), which confirms the formation of AuNCs with green emission properties. Also, the formation of AuNCs was monitored at different time intervals by fluorescence spectroscopy as shown in Fig. 3.

![Fig. 2](a) UV–visible spectra of NaCysC capped AuNCs synthesized below (curve a) and above the CMC (curve b). The inset shows the emission spectra of AuNCs when excited at 370 nm

Initially, no emission peak was observed in the reaction mixture. However, irradiation of UV light for 20 min, the reaction mixture exhibits green emission with low intensity indicates the formation of AuNCs. The intensity fluorescence gradually increased at 520 nm without any shift in the emission maxima when the solution was irradiated up to 5 h. Soon after no significant change in the fluorescent intensity was noted upon further extending the irradiation time. This observation clearly indicates that the reaction was completed within 5 h. Besides, the synthesized AuNCs were exhibit stability for more than 6 months and hence tested for their applications as a fluorescent probe for the detection of metal ions.

**Morphological Studies of NaCysC Capped AuNCs**

The self-assembling behaviour of NaCysC was confirmed by microscopic studies. Figure 4a, b shows the low and high magnification FE-SEM images of NaCysC at above the CMC in aqueous medium where the molecules are formed as aggregated form could be due to the hydrophobic and hydrophilic interactions. High resolution transmission electron microscope (HR-TEM) was used to characterize the morphology of AuNCs and their size distribution was observed using dynamic light scattering (DLS) studies. The HR-TEM micrographs of NaCysC stabilized AuNCs with different magnifications are depicted in Fig. 4c, d at above the CMC wherein the spherical shaped ultra-small sized particles having size < 3 nm with was observed. Further the hydrodynamic radii of NaCysC capped AuNCs was measured using DLS analysis and found to be yielding 3.9 ± 0.4 nm (inset of Fig. 4d). The difference in the HR-TEM and DLS measurement could
be due to the fact that DLS measurements records higher values, since the light scattered from both core particle as well as layer on the surface of the NCs. Whereas in HR-TEM measurement only the metallic particle core is measured. The interactions of NaCysC functional groups on the surface of metal NCs has been studied by FT-IR spectroscopy. The changes in the shape and peak position after the formation of AuNCs was compared with pure NaCysC as shown in Fig. 5. In pure NaCysC, the peaks appeared at 3381, 2561, 1636, 1518 and 1453 cm\(^{-1}\) corresponds to the stretching vibration of –OH and –NH group, SH, \(-C=O\), \(O=C-NH\), and COO– groups respectively. After the stabilization of AuNCs, the intensity of -SH peak is completely vanished indicating the binding of SH group on the surface of NCs. Also, the characteristic frequency of –NH, \(C=O\), and COO- are shifted towards higher frequency which confirms the interaction functional groups on the NCs surfaces.

**Fig. 4** FE-SEM image of NaCysC at above the CMC with different magnification (a & b) and HR-TEM images of NaCysC stabilized AuNCs with different magnifications (c & d) and its corresponding particle size distribution of AuNCs (inset of d)

**Fig. 5** FT-IR spectra of pure NaCysC (a) and NaCysC stabilized AuNCs (b)
Fig. 6 Fluorescence spectra of NaCysC capped AuNCs in the presence of different heavy metals ions. (a) The bars represent the fluorescence intensity ratio ($F/F_0$) of AuNCs incubated with different metal ions (b).
Metal Ions Recognition Ability of NaCysC Capped AuNCs

In recent years AuNCs were extensively used as fluorescent probe for the sensing of heavy metal ions because the intensity of fluorescence significantly altered in the presence of analytes. Therefore, the synthesized green emitting AuNCs was tested as fluorescent probe for the detection of heavy metal ions such as Na⁺, K⁺, Ca²⁺, Li⁺, Cd²⁺, Hg²⁺, Fe²⁺, Co²⁺, Cr³⁺, Cu²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ at fixed concentration in aqueous medium and the changes in the emission intensity was monitored by fluorescence spectroscopy as shown in Fig. 6a. After the addition of 70 μM of metal ions with AuNCs, the solutions were incubated for 10 min then the changes in the emission peak was monitored upon excitation at 370 nm. Among the various metal ions tested, only the addition of Hg²⁺ ions quenches the fluorescence intensity about more than 80% in presence of 70 μM of Hg²⁺ ions, while the rest of the metal ions no substantial change in the fluorescence intensity was observed (Fig. 6b). The greater the quenching effect of Hg²⁺ ions over the other environmentally relevant metal ions indicates the high specificity and selectivity of this probe towards Hg²⁺ ions detection.

Sensitivity Detection of Hg²⁺ Ions Using AuNCs

To evaluate the sensitivity of NaCysC capped AuNCs, various concentrations of Hg²⁺ ions such as 15, 30, 45, 60, 75, 90, 105, and 120 μM were added into the AuNCs solution. The intensity of fluorescence progressively quenched without any changes in the emission maxima at 520 nm and spectral shape upon increase in the concentration of Hg²⁺ ions as shown in Fig. 7a. This could be due to the coordinating ability of -SH group containing in NaCysC with Hg²⁺ ions and strong 5d₁₀–5d₁₀ metallophilic interactions between Hg²⁺ and Au⁺ on the surface of NCs, which leads to either destabilization or aggregation of NCs thereby the intensity of fluorescence quenched significantly [26]. A linear correlation obtained by plotting the value of (F₀-F)/F₀ and concentration of Hg²⁺ in the range from 15 to 120 μM with a correlation coefficient (R²) of 0.9926 (Fig. 7b). Where F₀ and F represent the fluorescence intensity of NaCysC capped AuNCs before and after the interaction of Hg²⁺ ions, respectively. The limit of detection (LOD) was found to be is 15 nM which is less than the maximum permitted level of Hg²⁺ in drinking water by the World Health Organization (WHO) and Chinese National Standard [39–41]. Also, the intensity of fluorescence completely quenched within 9 min after the addition of Hg²⁺ ions, which indicates that the synthesized NCs could be used as suitable probe for the detection of Hg²⁺ ion in aqueous environment. Scheme 2 represented the sensing mechanism of Hg²⁺ ions based on the quenching of fluorescence intensity of NaCysC stabilized AuNCs at 520 nm (turn off). Upon addition of Hg²⁺ into the NCs solution, there are two possible interactions between NCs with Hg²⁺ ions. The first one is NaCysC containing -SH group strongly interact with Hg²⁺ ions, thereby the capping molecules are removed on the surface of the NCs and the second possibility is that the Hg²⁺ ion has higher affinity to interact with AuNCs through strong 5d₁₀–5d₁₀ metallophilic interaction between Hg²⁺ and Au⁺ ions, resulting in fast adsorption of Hg²⁺ ion on the surface of AuNCs. Hence, the NCs becomes destabilized or aggregated owing to the removal of capping molecules and metallophilic interactions as shown in the Scheme 2. As a result, the intensity of fluorescence decreases upon increase in the concentration of Hg²⁺ ions.

Fig. 7 Fluorescence quenching of NaCysC capped AuNCs in presence of different concentrations of Hg²⁺ (a). Changes in the relative fluorescence (F₀-F)/F₀ as a function of Hg²⁺ concentrations at wavelength 520 nm (b)
Interference of Metal Ions

To evaluate the comparative test of individual metal ions with Hg$^{2+}$ ions, the changes in the emission spectra of AuNCs was monitored in the presence of competitive metal ions at fixed concentration (100 μM). The bar diagram in Fig. 8 shows the selectivity and sensitivity among other competing metal ions. The interference test clearly indicates that Hg$^{2+}$ ions efficiently quenches the AuNCs even in presence of other metal ions through strong 5d$^{10}$–5d$^{10}$ metallophilic interaction between Hg$^{2+}$ and Au$^+$ on the gold surface.

Conclusions

In conclusion, we have reported a simple, cost effective efficient and green approach for the synthesis of NaCytaC stabilized AuNCs with green emission properties in aqueous medium at above the CMC under UV light irradiation at 370 nm. Where NaCytaC act as effective template for the reduction and stabilization of NCs. The optical and morphological properties of NaCytaC capped AuNCs were studied by UV–visible, fluorescence spectroscopy FE-SEM, HR-TEM, DLS and FT-IR analysis. The synthesized AuNCs exhibit stable dispersion at basic pH (9.0) and
exhibit high stability at room temperature for more than six months. The prepared AuNCs having size less than 3 nm with distinct excitation and emission properties. Further the prepared AuNCs were used as fluorescent probe selective and sensitive detection of Hg²⁺ over other metal ions and the detection limit was found to be 15 nM. Hence, it could be effectively used as fluorescent probes for the sensing of metal ions in both environmental and biological samples.

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**Availability of Data and Material** The data that support the findings of this study are available from the corresponding author. (JK) upon reasonable request.

**Declarations**

**Ethical Approval** Not applicable.

**Consent to Participate** Not applicable.

**Consent for Publication** All the authors are consent to publishing the paper.

**Conflict of Interest** There is no conflict to declare in our manuscript.

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