Luminescent Au$_6$ and Au$_8$ nanoclusters from ligand induced etching of Au nanoparticles

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Keywords: nanocluster, luminescent, core etching  
Supplementary material for this article is available online

Abstract

Metal nanoclusters (NCs) with atomic precision are receiving significant attention because of their widespread applications in the field of energy-related materials, sensing and biomedicine. In this work, luminescent Au nanoclusters (NCs) are synthesized from Au nanoparticles (NPs) by core-etching process in presence of excess glutathione (GSH) ligand. Electrospray ionization (ESI) mass spectrometric study suggests the formation of polydisperse Au$_6$ and Au$_8$ NCs at elevated temperature (70 $^\circ$C). The HOMO-LUMO band gap of Au$_6$ and Au$_8$ clusters are calculated from optimized structure. The photoluminescence maximum of as-prepared Au NCs is observed at 421 nm after excitation at 340 nm with 4.20% quantum yield (QY). Lifetime of the NCs is found to be 0.57 ns in excited state, which arises because of electronic transitions from low-lying d-bands to excited state sp bands of core-state only. Moreover the luminescence intensity of as-prepared Au NCs is found to be very stable both in acidic and basic medium. The synthesis of luminescent Au NCs from non-luminescent plasmonic Au NPs is beneficial for various applications such as sensing, biomedicine, and light emitting devices.

1. Introduction

Significant attention has been given on synthesis of metal nanoclusters (NCs) for their unprecedented electronic and optical properties [1–7]. These nanoclusters or clusters have typical size around 2 nm [8, 9]. Au nanoparticles are well known for their size dependent surface plasmon resonance (SPR) whereas metal nanoclusters do not exhibit SPR band. The discrete electronic states of nanoclusters cause molecular like behavior, tunable optical properties which make them promising materials for applications in sensing, bio-imaging, cancer therapeutics, catalysis and light-emitting devices [3, 10–20]. The photoluminescence property of Au-nanoclusters is associated with the recombination of d-band electrons and it strongly depends on the number of metal atoms, nature of capping ligands, and pH [12, 21, 22]. Therefore, strategies have been taken for the synthesis of atomically precise metal clusters with tuning their optical properties. Generally, metal NCs are synthesized using thiol capping ligands owing to their greater capability to bind with noble metal surface [23, 24]. Usually, metal NCs are synthesized by two methods: either top down and bottom up approach [12]. In top down method, nanoclusters are prepared from large metal nanoparticles by excess etching ligands (mostly thiol ligands) [4]. Pradeep et al have synthesized metal nanoclusters by using etching with mercaptosuccinic acid (MSA). We have also reported blue and red emitting copper nanoclusters (Cu NCs) formation from copper nanoparticles (Cu NPs) in presence of excess glutathione [4]. In bottom up approach, nanoclusters are prepared by direct reduction of metal salt (Au$_3$$^{2+}$, Ag$^+$ and Cu$^{2+}$) using mild reducing agent (NaBH$_4$, CO, N$_2$H$_4$ etc) in presence of suitable capping ligands [25–28]. For example, Jin and his co-workers have synthesized monodispersed Au$_{144}$ NCs by reducing Au(I)-SR complexes in presence of excess NaBH$_4$ [29]. Dickson et al have reported the tunable emissive magic number Au-clusters with different numbers of Au-atom such as Au$_5$, Au$_7$, Au$_9$, Au$_{11}$.
Au10, Au113, Au25 and Au131 using PAMAM as a capping agent [5]. Xie et al have used BSA protein for synthesis of luminescent Au131 NCs with 6% QY [22]. Qian et al have synthesized monodisperse Au198 clusters from mixed size Au8 clusters (n = 38 to 102) in presence of excess phenylethythiol (PhC2H4SH) [30]. There are very few reports where metal NCs are being synthesized from larger size plasmonic nanoparticles.

Herein, we report the synthesis of highly luminescent Au6 and Au6 NCs using top-down method. The nanoclusters are synthesized from citrate capped plasmonic Au nanoparticles using excess glutathione via core-etching. We have optimized the structures of Au6 and Au8 NCs and calculated the HOMO–LUMO band gap by theoretical studies. The as-synthesized Au NCs exhibit blue emission (maximum 421 nm) with 4.20% QYs. The conversion of Au NPs (10 nm size) to ultrasmall Au NCs (<2 nm) is well investigated from UV−vis, PL and TEM analysis. Electrospray ionization (ESI) mass spectrometry has been used to investigate the composition of clusters i.e. number of metal atom and surface ligands. Mass spectrometric analysis and gel electrophoresis confirm the formation of mixture of Au6(SG)2, Au6(SG)3, Au8(SG)2, and Au8(SG)3 clusters. The as-prepared Au NCs may open up new possibilities for potential applications in sensing, bio-imaging, photocatalysis, and light emitting devices.

2. Experimental section

2.1. Materials

Tetrachloroauric acid trihydrate (HAuCl4·3H2O), glutathione reduced (GSH), trisodium citrate dihydrate were purchased from Sigma-Aldrich. Other chemicals, such as sodium borohydride (NaBH4) and sodium hydroxide (NaOH) were purchased from Merck. High purity water (~18.2 MΩ) was used for all the experiments. All the above mentioned chemicals of highest purity grade were used without further purification.

2.2. Synthesis of gold nanoclusters using top-down method

The luminescent Au NCs is synthesized by top-down method that involves ligand induced core-etching process. Initially, plasmonic nanoparticles were synthesized, which thereafter converted into fluorescent NCs.

2.2.1. Plasmonic gold nanoparticles synthesis

In a typical synthesis, 200 μl of AuCl4− (100 mM, HAuCl4·3H2O) is added to 10 ml of ultrapure water in a 20 ml beaker. Then, 200 μl of trisodium citrate (10 mg in 1 ml) is added to Au3+ solution and stirred for 5 min. After that, 200 μl freshly prepared icy cold NaBH4 (43 mg in 10 ml) is added drop wise to the reaction mixture. Immediately, after NaBH4 addition the color of the mixture changes from colorless to brown to red. The reaction is further continued for another 30 min for complete NPs formation and then the NPs are kept at 4 °C for further use.

2.2.2. Synthesis of blue-emitting Au NCs

1 ml of as-prepared Au NPs is taken in a 25 ml round bottom flask and 10 ml HPLC water is added. Then 307 mg GSH (a bio-active tripeptide) is added and the reaction is heated at 70 °C for 36 h. The reaction is monitored using UV−vis and PL spectroscopy. Finally, as-synthesized Au NCs are purified by centrifugation at 10000 rpm for 10 min.

2.3. Characterization

Transmission electron microscopy (TEM) images were recorded using a JEOL-JEM-2100F transmission electron microscope system. The UV−vis spectrophotometer (Shimadzu) was used at room temperature for absorption spectra. Photoluminescence spectra were collected using Fluoro Max-P (HORIBA Jobin Yvon) luminescence spectrophotometer at room temperature. SHIMADZU made FTIR-8300 spectrometer was used for infrared spectra using KBr pellets. Malveron Zetasizer instrument was used for the zeta potential and luminescence spectrophotometer at room temperature. SHIMADZU made FTIR-8300 spectrometer was used for absorption spectra. Photoluminescence spectra were collected using Fluoro Max-P. The UV−vis, PL and TEM−EDX analysis, the sample was excited at 340 nm using a picosecond NANO-LED IBH 340 L instrument. The full width at half-maximum (FWHM) of the system response using a liquid solution scatter was <1.2 ns. The fluorescence decay was collected on a Hamamatsu MCP photomultiplier. The experimental time−resolved fluorescence decays was analyzed using equation (1) [31]:

\[ p(t) = b + \sum_{i}^{n} \alpha_i \exp(-t/\tau_i) \]  

Here, n is the number of emissive species, b is the baseline correction (‘DC’ offset), and \( \alpha_i \) and \( \tau_i \) are, respectively, the pre-exponential factor and the excited-state fluorescence decay time associated with the ith component. The average decay time \( \langle \tau \rangle \) is estimated from equation (2) [31].
\[ \langle \tau \rangle = \sum_{i=1}^{n} \beta_i \tau_i \]  

(2)

Where \( \beta_i = \alpha_i / \sum \alpha_i \), and \( \beta_i \) is contribution of the decay component.

The QY of Au NCs was measured by comparison with reference dye, quinine sulphate (in water), by using the equation

\[ \text{QY}_{\text{F}} = \frac{(E F \times A F \times \eta F^2 \times \text{QY}_{\text{r}})}{(E \times A \times \eta^2)} \]  

(3)

Where, \( F \) and \( s \) are the integrated fluorescence emission of the reference and the sample. \( A \) and \( \eta \) are the absorbance at the excitation wavelength of the reference and the sample. \( \eta \) and \( \eta_f \) are the quantum yields of the reference and the sample, respectively. Quinine sulphate was used as a reference dye (QYF = 58%) to obtain the QYF of Au NCs. The refractive index for the sample and reference (\( \eta \) and \( \eta_f \)) of the solvent is 1.33 because water is used for both the cases. A Spectroline E-Series UV lamp source with 365 nm excitation wavelength was used to capture the picture under the UV exposure. High resolution mass spectra were recorded on Waters Q-Tof micro MS system by electrospray ionization (ESI) technique. The native polyacrylamide gel electrophoresis (PAGE) was carried out for the Au NCs and the resolving gel and staker gel were prepared by TGX stain free Bio-rad acrylamide resolver and staker solutions. The crude solution of Au NCs (10 μl of Au NCs in 6 vol % glycerol) was loaded onto the wells of staking gel. As eluting buffer, tris-glycine buffer consisted of 192 mM glycerine, and 25 mM tris(hydroxymethyl)amine was used. The electrophoresis process was allowed to run for 90 min at a constant voltage of 100 V. During the gel electrophoresis, temperature of the PAGE setup was kept at ice-cold. After successful run, the picture of wet gel was taken under UV illumination (365 nm).

2.4. Methods and computational details

All the calculations for electronic structure have been carried out using the Gaussian 09 [32] suite of quantum chemistry program. M06L [33, 34] hybrid functional in conjunction with LANL2DZ [35–37] basis set has been employed for optimizing the geometries of nanoclusters. HOMO-LUMO gap has been further calculated from the optimized structures.

3. Results and discussion

Citrate capped Au NPs are synthesized from aqueous solution of Au3+ salt by using mild reducing agent(NaBH4) at ambient temperature. A sharp surface plasmon resonance band at 519 nm in UV–vis absorption profile confirms the formation of Au NPs (figure 1(A)) [11]. The size of Au NPs is investigated using transmission electron microscopy (TEM) and it is clearly observed from the image that the size of spherical Au NPs is around 10 nm (figure 1(B)). Then, Au NPs is etched with excess glutathione ligands (a bioactive tri-peptide, consisting with L-cysteine, L-glutamic acid, and glycine) at 70 °C (figure S1 is available online at stacks.iop.org/MRX/6/124004/mmedia). The color of Au NPs solution turns to violet from red immediately after addition of excess GSH (1 mmol, 307 mg) (scheme 1). The replacement of citrate ligands by GSH from the surface of NPs brings them closer and they form a large aggregated structure which causes the change in color [38, 39]. The SPR band of as-prepared Au NPs shifts from 519 nm to 582 nm within few seconds due to the formation of larger Au NPs aggregates (figure 1(C)).

The Au NPs become aggregated just after the addition of GSH that is clearly visible from the TEM image (figure 1(D)). Furthermore, the formation of aggregation is confirmed from DLS size measurement where the hydrodynamic size of Au NPs is enhanced from 107 to 390 nm just after addition of GSH (figure S2). Citrate ions are bound to Au atoms via oxygen atoms and citrate ligands are replaced by thiolate ligands with the formation of Au-S bonds [4]. The etching of Au NPs is monitored by UV–vis absorption and photoluminescence spectroscopy (figure 2). After 30 min of etching at 70 °C, the SPR band is further shifted to red end at 630 nm (figure 2(A)). As the Au-S bond is very stable, the binding of GSH causes such change in color. Ligand assisted etching is continued at 70 °C and the color of the reaction medium vanishes after 30 min. Finally, the plasmonic band of Au NPs is completely disappeared after 6 h of etching. A new peak appears at around 337 nm, and the peak becomes prominent as the course of reaction increases from 6 h to 24 h (figure 2(A), curve d).

The plasmonic band is completely disappeared after 36 h core-etching of Au NPs and the new absorption bands observed at 337 nm and 392 nm which are due to electronic transitions (figure 1(E)) [3, 13, 40]. The luminescence intensity of Au NCs is appeared after 12 h of etching and the maximum intensity is observed after 36 h (figure 2(B)). The as synthesized blue emitting Au clusters exhibit size below 2 nm, indicates the formation of nanoclusters (figure 1(F)) [3, 41]. Therefore, the successful reduction of core size from 10 nm to 2 nm suggests the formation of nanoclusters from nanoparticles by glutathione assisted core-etching. During the GSH-regulated etching of NPs, GSH are supposed to bind with the surface of Au NCs via the Au-S covalent bond formation, which is confirmed from fourier transform infrared (FTIR) spectroscopy (figure S3). Pure GSH ligand, exhibit a characteristic peak 2524 cm⁻¹ which arises due to the presence of free –S–H moiety. This peak is
Figure 1. Absorption spectra and TEM images of Au NPs (A), (B), Au NPs-GSH (C), (D) and GSH-capped Au NCs (E), (F), respectively.

Scheme 1. Schematic illustration of Au nanoparticles to Au nanoclusters conversion via top-down method (top row). Digital pictures of solid Au nanoclusters under visible and UV-light.
completely disappeared in GSH-capped Au NCs, suggesting the formation of Au-S covalent bond. All other characteristics peaks remain same in NCs, which further confirms the binding of GSH to NCs surface.

It is interesting to note that no fluorescence band appears if the etching process is done out at room temperature (25 °C) except the shifting of the plasmonic band from 519 nm to 647 nm even after 36 h (figure S4). Thus, we can say that the etching of Au NPs is not feasible at room temperature that occurs at elevated temperature (70 °C). The exact feeding ratio of GSH to NP is obtained by performing different sets of experiment and monitored by UV and PL spectroscopy. Excess GSH of 1 mmol (307 mg) is allowed to interact with 1 ml of citrate capped Au NPs for core-etching (figure S5).

It is noted that no luminescence is observed (figure S6) from glutathione after heating at 70 °C for 36 h, indicating the luminescence appears from metal clusters only not from ligands. The influence of pH on Au clusters formation is investigated and it is seen that the pH of the reaction medium has a remarkable effect on the luminescence of Au NCs. The maximum PL intensity of Au clusters is found at pH = 1 compared to pH = 3, pH = 5 and pH = 9 (figure S7).

Electrospray ionization mass spectrometry (ESI-MS) analysis is being used for the identification of molecular composition of as-synthesized Au NCs. Figure 3(A) shows a series of peaks at m/z 1397 (d), 1223 (c), 1093 (b) and 917 (a) in the range of 800–2000. Inset of figure 3(A) reveals the zoomed view of mass spectrum and the peaks are assigned to \([\text{Au}_{6}(\text{GSH})_{4}-2 \text{H}]^{2-}\), \([\text{Au}_{8}(\text{GSH})_{2}+2\text{Na}^{+}-4 \text{H}]^{2-}\), \([\text{Au}_{8}(\text{GSH})_{2}-2 \text{H}]^{2+}\), \([\text{Au}_{4}(\text{GSH})_{2}+2\text{Na}^{+}-4 \text{H}]^{2-}\), respectively. Therefore, glutathione directed etching of Au NPs produce mixture of four different sized clusters. In addition, a native polyacrylamide gel electrophoresis (PAGE) analysis of as-prepared Au NCs shows three distinguishable luminescent band under UV illumination, confirms the mixture of three different luminescent species (figure 3(B)). Three bands (band1, band2 and band3) exhibit three different emission colors, suggesting the mixture of Au NCs and one of the clusters may have very low quantum yield or non-luminescent. Figure 3(C) reveals the luminescent intensity of Au NCs after gel separation and the PL intensity of band 1 is higher compared to band 2 and band 3.

We are able to optimize three structures of \(\text{Au}_{6}(\text{GSH})_{2}\), \(\text{Au}_{8}(\text{GSH})_{1}\), \(\text{Au}_{8}(\text{GSH})_{1}\), where all the structures are in neutral form, the optimized structures are depicted in figure 4. But we do not get any optimized structure of \(\text{Au}_{8}(\text{GSH})_{2}\) rather we find optimized structure of \(\text{Au}_{8}(\text{GSH})_{1}^{2-}\). For all the cases, the associated clusters are significantly distorted and do not form any well defined symmetric structure. The GSH ligands are ligated through sulfur end to Au clusters. For \(\text{Au}_{6}(\text{GSH})_{2}\) cluster, two GSH are attached to Au6 cluster from almost opposite side. The GSH ligands are connected through H-bonding through their –COOH groups. For \(\text{Au}_{8}(\text{GSH})_{2}\) cluster, the GSH ligands bind through opposite side but the ligands are not interacted with each other. In \(\text{Au}_{8}(\text{GSH})_{4}\) clusters, GSH ligands are connected with each other through H-bonding interaction between –COOH and –NH2 groups. For \(\text{Au}_{8}(\text{GSH})_{2}^{2+}\) cluster is surrounded by four ligands and the ligands are interacted with each other through H-bonding interaction between –COOH and –NH2. We have further calculated HOMO-LUMO band gap of all the Au NCs (table 1).

It is observed that both \(\text{Au}_{6}(\text{GSH})_{2}\) and \(\text{Au}_{8}(\text{GSH})_{2}\) complex have similar HOMO-LUMO gap and also matches with experimental results. The band gap of \(\text{Au}_{6}(\text{GSH})_{4}\) is much less than that of experimental value whereas the gap for \(\text{Au}_{8}(\text{GSH})_{2}^{2+}\) is much higher than experiment. This HOMO-LUMO band gap is comparable with other band gap [3, 30].

The excitation spectrum of Au NCs shows three distinctive peaks at 300 nm, 350 nm and 395 nm, which are well matched with the absorption band (figure 5(A), a curve). The as-prepared Au NCs exhibit blue emission peak centered at 421 nm (figure 5(A), b curve). Inset displays digital picture of GSH-capped Au6,8 NCs under
visible light and UV light. Interestingly, the synthesized Au NC exhibit 4.20% quantum yield as compared with quinine sulfate. In addition, the as-synthesized Au NCs exhibits excitation wavelength dependent luminescence property.

Figure 3. (A) ESI-MS spectrum of Au NCs, inset exhibits the zoomed view. (B) Digital picture of wet gel after PAGE at room temperature. (C) PL spectra of different luminescent bands after gel separation.

Figure 4. Optimized geometry of the Au₆ and Au₈ nanoclusters at M06L/LANL2DZ level.
The Au NCs is excited over wavelength range 280–400 nm to understand the optical heterogeneity. When the sample is excited between 280–360 nm, the emission maximum is observed at 421 nm. Interestingly, the emission maximum is found to be red shifted to 435 nm and 445 nm upon excitation at 380 nm and 400 nm, respectively (Figure 5(B)), indicating the existence of heterogeneity of Au clusters which is generally observed in metal NCs [42, 43]. Again the wavelength dependent PL emission of Au NCs is well agreed with the excitation band of Au NCs (Figure 5(A), curve a). Three different emission centers may be due to the mixture of three luminescent Au clusters, which is already illustrated from PAGE analysis. Furthermore, 75 nm Stokes shift is observed which is comparatively lower than other metal nanoclusters [3, 12]. This lower Stokes shift suggests that the fluorescence is originated from the core states of clusters not from the surface semi-ring states or ligand to metal charge transfer (LMCT) [12, 44]. To understand this phenomenon, the excited state lifetime is measured under the excitation of 340 nm and the emission is monitored at 421 nm (Figure 5(C)). The lifetime is found to be tri-exponential decay curve with the components of 0.21 ns (63%), 1.05 ns (35%) and 3.74 ns (2%) and the average lifetime is 0.57 ns. All three lifetime components are in the nanosecond time range which suggests that luminescence is originated from the electronic transitions of lower energy d-bands to higher energy sp bands of core-state only [12, 40]. Furthermore, we did not observe any microsecond lifetime components.
which was evident for blue emitting Au clusters \([40]\). Moreover, the luminescence intensity of as-synthesized Au NCs is very stable in the range of pH from 1.0 to 12.0 (figure 6) whereas the change in luminescence intensity with changing the pH is reported due to change of the ligand structure \([45, 46]\). Thus, this as-synthesized Au NCs could be useful for potential applications such as optical sensing, bio-imaging, catalysis and energy harvesting.

4. Conclusions

In summary, we have reported a top down synthesis method for the synthesis of highly luminescent blue emitting Au nanoclusters using plasmonic Au NPs as precursor. In this aqueous phase synthesis, first citrate capped Au NPs is synthesized by reducing \(\text{Au}^{3+}\) with \(\text{NaBH}_4\). Then luminescent Au NCs are prepared by core-etching of as-prepared Au NPs in presence of excess glutathione at elevated temperature \((70 \, ^\circ\text{C})\). The conversion mechanism of Au NPs to Au NCs is investigated in detail using various experimental tools such as UV–vis, PL, and TEM. The composition of atom and ligand is estimated from ESI mass spectroscopy (\(\text{Au}_6\) and \(\text{Au}_8\) NCs). Both the \(\text{Au}_6\) and \(\text{Au}_8\) NCs are optimized and HOMO-LUMO band gaps are estimated which are well matched with experimental results. The as-synthesized \(\text{Au}_{6, 8}\) NCs exhibits photoemission at 421 nm with 4.20% QYs and possesses nanosecond lifetime in excited states. Moreover luminescence intensity of as-prepared Au NCs is very stable both in acidic and basic medium. This newly developed synthesis protocol may be useful for the synthesis of other luminescent NCs (Ag NCs, Cu NCs) with reasonable QYs and also can be useful for various applications like sensing, bio-imaging, photocatalysis, photovoltaic, and light emitting devices.

Acknowledgments

‘DST-TRC’ and SERB-DST are gratefully acknowledged for financial support. DB and SM thank CSIR for awarding fellowships. We thank IACS for support throughout our investigation.

Conflict of interest

The authors declare no conflict of interest.

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