



The plasmonic behaviours of gold nanoparticles with different thiol ($n = 6, 10, 12$) capping agents

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Abstract

The intense absorbance and scattering of incident light at the surface plasmon resonance wavelength of gold nanoparticles (AuNPs) is of paramount importance in its various and diverse applications. Being governed by their morphologies and surface chemistry, the optical property of AuNPs can be tuned to suit variety of applications by careful and systematic engineering of the particle surface. Among other variables, the nature of the ligands or capping agents employed and their concentrations play vital roles. Three different alkanethiols, namely 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT) were investigated as capping agents in different concentration of gold/thiol ($[Au]/[Thiol]$) ratios of 7:1, 5:1, 3:1, 1:1, 1:3 and 1:5. First, the AuNPs with average particle sizes of 2 nm and characterised by ¹H NMR, UV–visible, and TEM. The ¹H NMR confirmed the capping of gold nanoparticles by the thiol. The TEM image confirmed the monodispersity of the nanoparticles with average size distributions of 2.4 nm, and plasmon absorption wavelength peaks at 505 nm was confirmed by the UV. There were variations in the values of the plasmonic peaks with the nature and concentrations of the capping agents.

Keywords Plasmon · Gold nanoparticles · Capping agents · Alkanethiols · Absorption

1 Introduction

Researchers are more interested in the nanoscience and nanotechnology nowadays than ever before due to production and characterization of new materials with remarkable properties for diverse applications. These nanomaterials proven to have diverse properties different from their bulk size counterpart [1]. Among other metals, gold nanoparticles (AuNPs) are the most investigated due to their unique properties, ease methods of synthesis, chemical stability and processability. Au nanostructures have unique and interesting mechanical, magnetic, electrical and optical behaviours which are totally different from their conventional macro- or millimetre size materials.

These properties rely hugely on their corresponding sizes, shape, surface chemistry and topology.

Nanomaterials are found to be practically applied in some of these areas but not limited to display (flat panel), magneto-optical discs, computer chips, sensors, non-volatile memories, insulators, catalysts, batteries, colour imaging, printing, photodetectors, solar cells, holography, optoelectronics, transistors and switches, medicine (drug delivery, implant, pharmacy) and cosmetic [2, 3]. Gold nanoparticles (AuNPs) are known for their localized surface plasmon resonance (LSPR) that can be easily detected and measured by UV–visible spectroscopy [4, 5]. The SPR band characteristics such as position, amplitude, and width peak depend strongly on the geometric characteristics (size,

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shape, and concentration) of the nanoparticles, as well as the nature of the surrounding medium [6, 7]. Gold can exist in various oxidation states, namely, 5, 4, 3, 2, 1, 0, – 1. Gold 3 is a strong oxidizing agent which is reduced to gold 1 in the reaction to synthesise gold nanoparticles [8, 9]. Thiolated ligands are often used to stabilize gold 1 due to its preferential reaction with Sulphur. The most preferable state for nanoparticles is the non-oxidized state (Au^0). In other words, the synthesis of AuNPs can be summarized as the reduction of positively charged gold nanoparticle aureus (Au^{+1}) or auric (Au^{+3}) to Au^0 by reducing agent with intense stirring to form fairly uniform NPs in size. Stabilizing medium that adsorbs on the surface of the NPs can be used to minimize their aggregation [9–11]. This same principle was applied to all the methods of NP production.

We report here the synthesis and the determination of the plasmonic behaviour of AuNPs capped with 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT) in different concentration of gold/thiol ($[\text{Au}]/[\text{Thiol}]$) ratios of 7:1, 5:1, 3:1, 1:1, 1:3 and 1:5. Table 1 shows the volume requirement for each molar ratio of the ligands considered.

2 Results and discussion

2.1 1-Decanethiol capped gold nanoparticles

The gold nanoparticles were characterised by ^1H NMR, TEM, UV–vis.

Figures 1 (a) and (b) show the ^1H NMR spectra of free 1-dodecanethiol and gold nanoparticle capped with 1-dodecanethiol respectively

The quartet signal due to $-\text{CH}_2\text{SH}$ in free thiol ($\delta = 2.50$ ppm) in spectrum (b) is broader than in spectrum (a) (triplet) due to $-\text{CH}_2\text{S}-\text{Au}$ formation. The signal due to ($-\text{SH}$) at $\delta = 1.29$ ppm in free thiol (a) has disappeared in capped AuNPs (b), confirming the thiol group chemically attached to the gold cores.

Table 1 Volume requirement for each molar ratio of the ligands

| Entry ([Au]/ [Thiol]) | DDT (Volume, μl) | DT (Volume, μl) | HT (Volume, μl) |
|-----------------------------|------------------------------|-----------------------------|-----------------------------|
| A (7:1) | 0.34 | 0.30 | 0.20 |
| B (5:1) | 0.45 | 0.41 | 0.28 |
| C (3:1) | 0.79 | 0.69 | 0.46 |
| D (1:1) | 2.38 | 2.07 | 1.40 |
| E (1:3) | 7.14 | 6.21 | 4.21 |
| F (1:5) | 11.90 | 10.36 | 7.02 |

The TEM image of the AuNPs synthesised is as shown in Figure 2.

The images confirmed the monodispersity of the AuNPs. Figure 3 shows the size distribution of the AuNPs as observed on TEM.

The minimum size obtained was 2.13 nm while the maximum value was 2.78 and with average value of 2.34 ± 0.16 nm. The relatively small values of the standard deviation clearly showed that the AuNPs are monodispersed.

The UV–vis spectra of the AuNPs are given in Figure 4 (a), (b) and (c).

The plasmonic behaviours of the 1-dodecanethiol (DDT) capped AuNPs, 1-decanethiol (DT) capped AuNPs and 1-hexanethiol (HT) capped AuNPs are respectively shown in Table 2.

There was a red shift from 540 to 550 nm in the surface plasmonic behaviour of DDT (entry A, $[\text{Au}]/[\text{Thiol}] = 7:1$), followed by a blue shift from 550 to 545 nm for entry B, meaning that the maximum amount of the ligands or capping agents have been accommodated onto the surface of the AuNPs. Hence, an attempt to add to the saturated surface resulted in the formation of slurry or colloid which made the purification and analysis difficult.

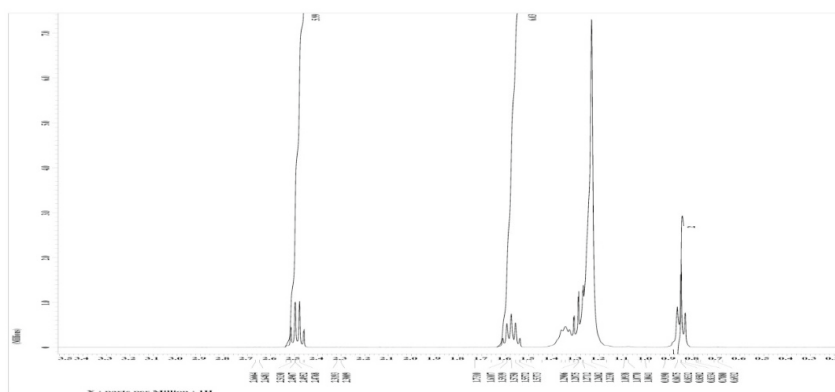
For DT, there was red shift from 560 to 545 nm for entry A ($[\text{Au}]/[\text{Thiol}] = 7:1$). There was further red shift of from 545 to 540 nm for entry B ($[\text{Au}]/[\text{Thiol}] = 5:1$). With further reduction of the $[\text{Au}]/[\text{Thiol}]$ ratios, no remarkable change in the value of the plasmon (540 nm) was observed.

HT showed absorption at 555 nm for the first entry A ($[\text{Au}]/[\text{Thiol}] = 7:1$). For $[\text{Au}]/[\text{Thiol}] = 5:1$, there was no well-defined absorption point but there was a well-defined value of 545 nm for the ratios $[\text{Au}]/[\text{Thiol}] = 3:1$ and 1:1. Further decrease in the ratio gave a red shift of 5 nm (540 nm). When compared, the plasmon absorption wavelength for DDT, DT and HT were 540 nm, 560 nm and 555 nm. It could be seen that the larger the size of the capping agent, the more the ratio of $[\text{Au}]/[\text{Thiol}]$, the more clearly define the plasmon absorption wavelength.

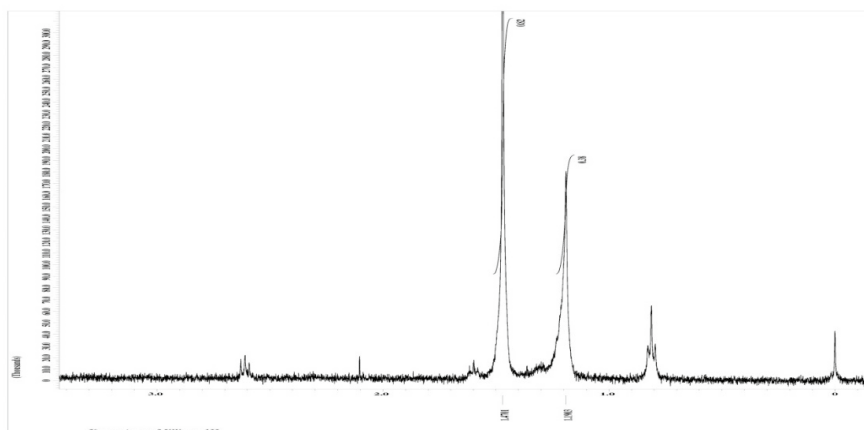
3 Conclusion

There are variations in the plasmonic behaviours of the AuNPs capped with different alkanethiols and this would be beneficial to their practical applications. This work demonstrated that the minimum values of $[\text{Au}]/[\text{Thiol}]$ ratio for 1-dodecanethiol, 1-decanethiol and 1-hexanethiol were found to be 5:1, 3:1 and 7:1 respectively with corresponding plasmonic peaks of 550 nm, 540 nm and 555 nm. At lower ratio, the values appeared either as a spec or not clearly defined. This work provided a guide in choosing the types and the amount of capping agents,

Fig. 1 **a** ^1H NMR spectra of free 1-Dodecanethiol. **b** ^1H NMR spectra of gold nanoparticle capped with 1-Dodecanethiol

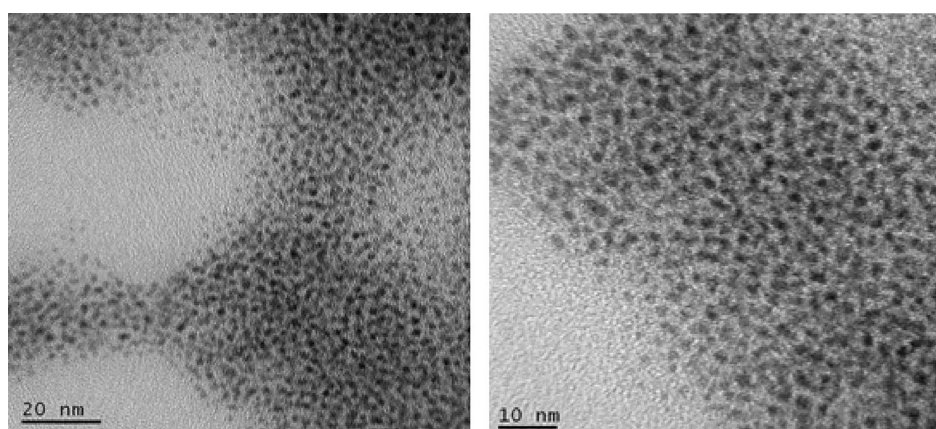


(a): ^1H NMR spectra of free 1-Dodecanethiol



(b): ^1H NMR spectra of gold nanoparticle capped with 1-Dodecanethiol

Fig. 2 TEM images of AuNPs



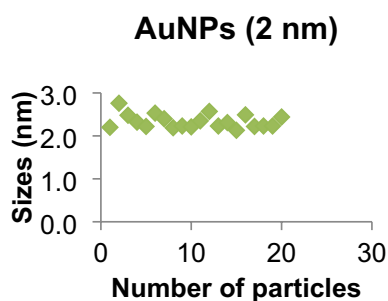


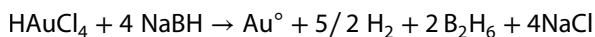
Fig. 3 Size distribution of the AuNPs

based on the [Au]/[thiol] ratio and their corresponding plasmonic peak values, required in the synthesis of AuNPs for varieties of applications.

4 Experimental

4.1 Gold Nanoparticles synthesis [12–15]

The gold nanoparticles were synthesised by the reduction of chloroauric acid (HAuCl_4) by sodium borohydride (NaBH_4) and subsequently capping (protecting) them with thiol based-ligand/stabilizer (alkanethiols).



The procedure involves the preparation of stock solutions of chloroauric acid and that of sodium borohydride as described below.

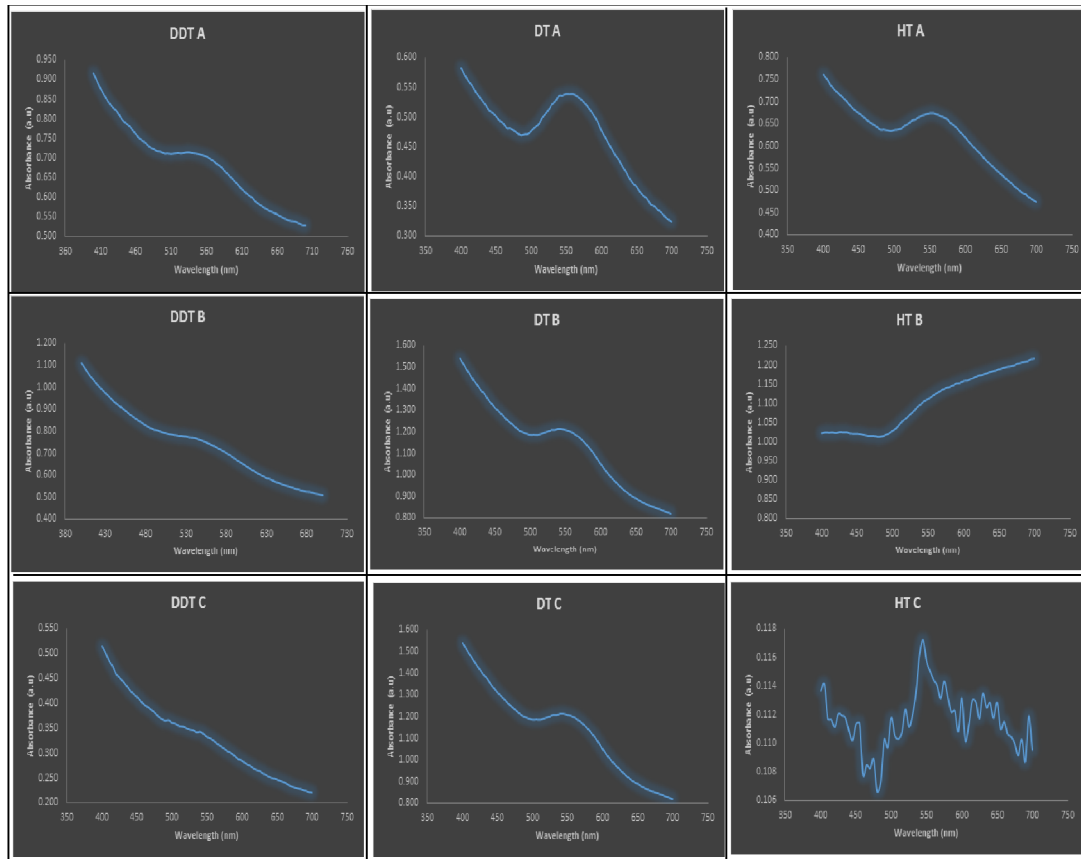
4.2 Stock solutions and nanoparticles preparations [16, 17]

Chloroauric stock solution (Stock **A**) was prepared by dissolving 0.17 g of HAuCl_4 (0.5 mmol) in 5 ml water. To this was added 0.032 ml concentrated hydrochloric acid and the solution briefly sonicated. The stock solution A was kept in the dark until when required.

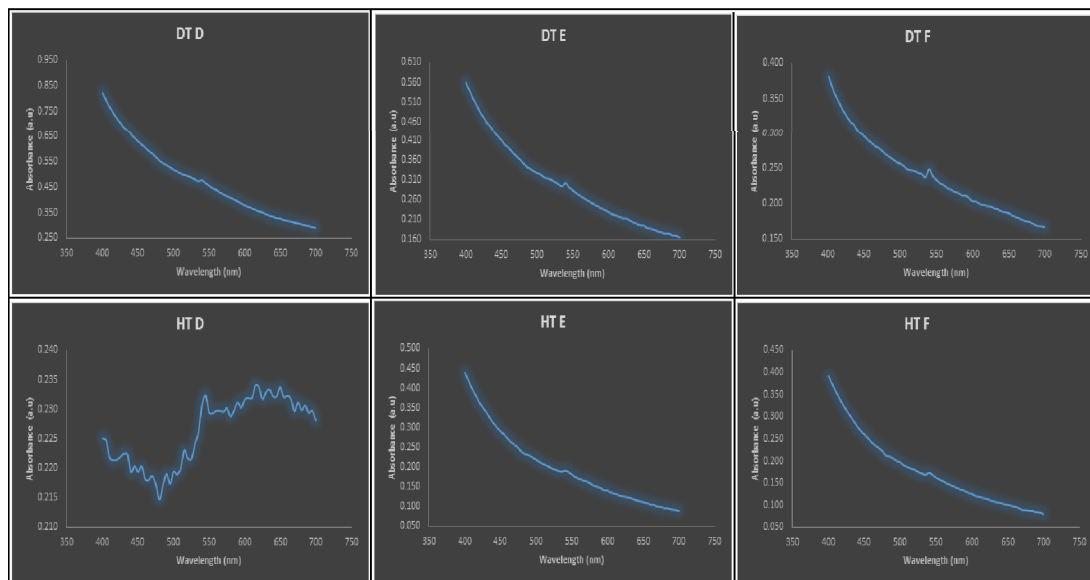
Borohydride stock solution (Stock **B**) was prepared by dissolving 0.03 g of sodium borohydride (0.8 mmol) and 0.03 g of sodium hydroxide NaOH (0.75 mmol) in 3.23 ml water and briefly sonicated.

To prepare the AuNPs Fig. 5, 100 μl of stock **A**, 20 μl of 1-dodecanethiol (**DDT**) (0.084 mmol) and 5 ml THF were mixed and sonicated. To the mixture was added 30 μl of stock **B** with further 10 min sonication. Excess solvent was removed *in vacuo* while the residue redispersed in ethanol for excess/unreacted DDT removal. The mixture was finally centrifuged at 5000 rpm for 5 min after which the supernatant was removed and the process repeated three times. The black DDT capped AuNPs residue was dried *in vacuo* and characterised.

The gold to thiol [Au]/[Thiol] ratios of 7:1, 5:1, 3:1, 1:1, 1:3 and 1:5 was subsequently used for the DDT, 1-decanethiol (**DT**) and 1-hexanethiol (**HT**) respectively, following the above procedure while keeping the gold to borohydride [Au]/[BH_4] ratio constant at 3:1. The volume requirement for each thiol molar ratio is as shown in Table 1.



(a): Plasmonic behaviour of entries A, B and C for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT).



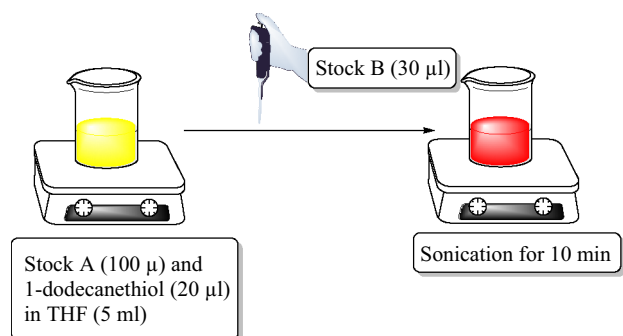
(b): Plasmonic behaviour of entries D, E and F for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT).

Fig. 4 a Plasmonic behaviour of entires A, B and C for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT) **b** Plasmonic behaviour of entires D, E and F for 1-dodecanethiol (DDT), 1-decanethiol (DT) and 1-hexanethiol (HT)

Table 2 Maximum wavelength (nm) for corresponding AuNPs

| Entry | DDT (λ_{max} , nm) | DT (λ_{max} , nm) | HT (λ_{max} , nm) |
|-------|------------------------------------|-----------------------------------|-----------------------------------|
| A | 540 | 560 | 555 |
| B | 550 | 545 | Φ |
| C | 545 | 540 | 545 |
| D | – | 540 ^a | 545, 620 |
| E | – | 540 ^a | 540 ^a |
| F | – | 540 ^a | 540 ^a |

Φ = Not clearly defined. ^a = Appeared as a speck. —not determined

**Fig. 5** Schematic representation of AuNP preparation

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Author contributions The project conception and design were done by GM and OA. Material synthesis, analysis, data collection and interpretations were performed by all authors. The first draft of the manuscript was written by OA. All authors read and approved the final manuscript.”

Data availability The data are available if needed.

Declarations

Conflict of interest The authors declare that there is no known competing interest that could have influence the work reported in this paper.

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