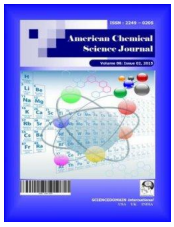

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Laboratory Preparation of the Precursor for Synthesis of Gold Nanoparticles

O. D. Ogundare[1*], M. O. Adeoye[2] and A. R. Adetunji[2]

[1]Engineering Materials Development Institute Akure Nigeria.
[2]Department of Materials Science and Engineering, Obafemi Awolowo University, Ile- Ife, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Authors ODO and MOA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ARA and MOA managed the analyses of the study. Author ARA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The synthesis of gold nanoparticles was investigated via the laboratory preparation of the precursor from the precipitated gold using sodium cyanide (NaCN) and cyanide solution from cassava. Characterization studies are carried out using TEM and XRD. The synthesis of gold nanoparticles was carried out using citrate reduction method as modified for the purpose of this research. TEM images reveal that spherical shaped and well-dispersed gold nanoparticles in the size range between 18 nm – 24 nm were produced successfully. The XRD confirm the crystallinity of the gold nanoparticles.

Keywords: Gold; chemical synthesis; nanostructure; structural properties.

**Corresponding author: E-mail: suppiedee@yahoo.com;*

1. INTRODUCTION

The last few decades have witnessed the emergence of nanotechnology as a promising field since it deals with nanoparticles displaying unique optical [1], electronic [2], chemical [3], photoelectrochemical [4] or magnetic properties [5] which render them to be applied for diverse functions. The foundation of nanotechnology is based on the size and shape of nanoparticles which play a significant role in tuning these properties. Indeed, the similarity of the size of nanoparticles to that of biological molecules (like proteins and DNA) along with bacteria and viruses has sprouted enormous interest in exploiting nanoparticles for various biomedical applications. Moreover, it has been proposed recently that the uptake of nanoparticles by mammalian cells is size-dependent [6]. This makes the study of the size of nanoparticles of utmost importance.

Owing to the diverse properties exhibited by gold nanoparticles (GNPs) [7], they bear applications in various areas such as cosmetics [8], electronics [9], therapeutics [10,11], imaging [12,13], drug delivery [14,15] and pollution remediation [16,17]. However, applications in such diverse fields often require GNPs to be of a particular size and be in large numbers or higher concentrations [18,19]. Hence, it becomes relevant to study the effect of changes in synthesis procedures on nanoparticle properties including size. The synthesis of GNPs mediated by citrate reduction of gold chloride solution is well documented [20-22]. Citrate molecules act as both reducing and stabilizing agents, allowing for the formation of the colloidal gold [22]. The initial choice of precursor ($HAuCl_4$) and trisodium citrate concentrations determine the final GNPs' size and size distribution obtained. It was found that initial gold salt ($HAuCl_4$) and trisodium citrate concentrations and mixing rate are very important variables in the colloid nanoparticle synthesis [23]. It was reported that the average diameter and the character of the distribution curve changed with preparative conditions such as concentration and ratio of reactants.

In recent years, the increasing number of published papers shows great interest of engineers and scientists for the importance of metal nanoparticles (NPs) such as silver (Ag), gold (Au) and copper (Cu) etc., because of their physicochemical properties, nano meter (nm) size and surface plasmon behavior [24,25]. These metal NPs are used in catalysis, electronics for circuit development and as self-assembled new nanostructure materials, but only few show different sets of applications with light interaction. The interaction of light in a field with metal nanostructures is called as plasmonics [26-30]. The plasmonic nanostructure materials are defined by means of their strong interaction with incident light and free electrons, where metal nanostructures act as a source to convert light into localized electric field (electromagnetic excitations coupled with collective oscillations of free electrons) in metals [31], and called as localized surface plasmon. Incident light can work more effectively with strictly controlled size and shape of metal nanostructures [27,32].

Gold nanoparticles (AuNPs) are the most commonly synthesized nanomaterials by green chemistry approach as it is easy to synthesize due to its high reduction potential (1.51 eV) and easy to characterize by observing the ruby red coloration and by the characteristic surface plasmon resonance (SPR) of AuNPs (λmax: ~530-550 nm). It is worth mentioning that gold and its related compounds have been used for therapeutic purposes since ancient times. The medicinal importance of gold has also been explored in modern era involving a wide range of applications of AuNPs such as drug delivery, tumour imaging, cell tracking, anti angiogenic therapy, plasmonic photo thermal therapy etc. [33]. Various methods for preparation of metal nanoparticles have been summarized in Fig. 1 below:

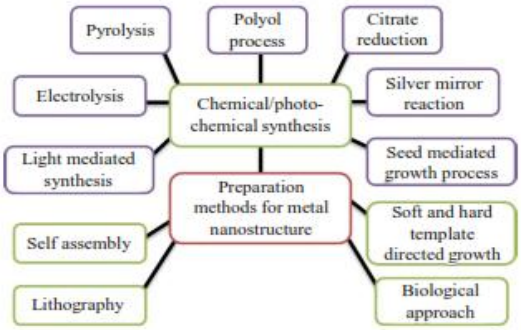


Fig. 1. Various preparation methods for metal nanostructure [34]

In the majority of the published citrate reduction works, it is interesting to note that the precursor used in the synthesis of GNPs is mostly sourced commercially. Information on the laboratory preparation of the precursor is very scanty or inaccessible in the literature. Hence, this work

has presented the laboratory preparation of the precursor.

2. EXPERIMENTAL

Gold nanoparticles [35] are usually synthesized by reduction reaction between analar grade hydrogen tetrachloroaurate ($HAuCl_4$) and trisodium citrate ($Na_3C_6H_5O_7$). The synthesis of gold nanoparticles was carried out using citrate reduction method as modified for the purpose of this research. Aqua Regia solution was prepared and the mixture was stirred and heated continuously for 30 minutes using the 78 HW-1 constant temperature magnetic stirrers. The mixture turned yellowish and was allowed to cool down. A known quantity of the precipitated gold obtained using cyanide solution from cassava was dissolved in the aqua regia in order to prepare hydrogen tetrachloroaurate ($HAuCl_4$) solution. 0.5 mM $HAuCl_4$ was prepared in some distilled water and standardized. 50 ml of 0.5 mM $HAuCl_4$ was poured in a beaker and heated to boil on a hot plate with magnetic stirrer. 0.5 g of trisodium heptaoxocitrate (V) oxide ($Na_3C_6H_5O_7$) was dissolved in some distilled water and made up to mark in order to prepare 38.8 mM $Na_3C_6H_5O_7$. To this boiling solution, 5 ml of $Na_3C_6H_5O_7$ was added in continuous mode quickly with simultaneous stirring. After addition of sodium citrate solution, stirring continued until solution turned colourless, then it darkened and later to brilliant purple colour. Finally, it turned to deep wine. Nanoparticle formations were detected by transparency observations and red wine coloured solutions.

The synthesis reaction is summarized as given below:

$$Au_{(s)} + HNO_{3(aq)} + 4HCl_{(aq)} \longrightarrow HAuCl_{4(aq)} + NO_{(g)} + 2H_2O_{(aq)} \quad (1)$$

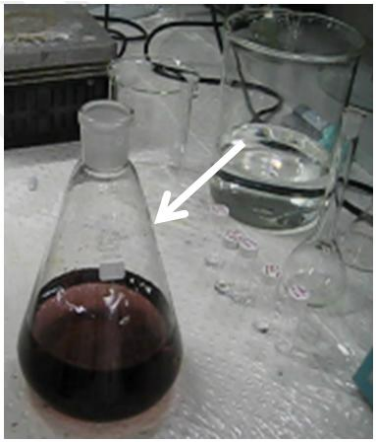
$$2HAuCl_{4\,(aq)} + 3C_6H_8O_{7(aq)} \longrightarrow 2Au_{(s)} + 3C_5H_6O_{5(aq)} + 8HCl_{(aq)} + 3CO_{2(g)} \quad (2)$$

This solution was stored at 4°C for further use. The procedure above was repeated using gold precipitated from analar sodium cyanide.

The size of gold nanoparticles has been determined by measuring the diameter of whole particles on TEM images. X-ray diffraction measurements of the films and powders in the present studies were carried out using Rigaku automated x-ray diffractometer. The filtered copper K_α (λ = 1.5418 °A) radiation was used for recording the diffraction pattern.

(a)

Fig. 2(a). Aqua Regia solution with dissolved gold precipitate



(b)

Fig. 2(b). Colour transition during gold nanoparticles formation

3. RESULTS AND DISCUSSION

The TEM images of synthesized gold nanoparticles from gold precipitated using sodium cyanide analar grade and cyanide solution from cassava are shown in Plate 1 and 2 respectively. The TEM images show that the gold colloid is in monodispersional state, this is because of negatively charged layer of citrate ions which repel from each other. This monodispersity accounts for the probe preparation and generation of color

signal in chromatographic strip assay. Moreover, the TEM images show that most of the gold nanospheres are round or spherical in shape. In the TEM image shown in Plate 1, the size range of the nanoparticles can be observed to be between 21-29 nm. The size of gold nanoparticles has been determined by measuring the diameter of three particles on TEM images. The average diameter of colloidal gold was in the range of 24.2 nm with few particles of higher size distribution. Also, it can be observed that the gold nanoparticles are dark spherical shaped dots with smooth surface morphology.

In the TEM image shown in Plate 2, the size range of the nanoparticles can be observed to be between 13-24 nm. The size of gold nanoparticles has been determined by measuring the diameter of five particles on TEM images. The average diameter of colloidal gold was in the range of 18.2 nm with more particles of lower size distribution. This work is in agreement with the work of [35] who obtained 18 nm from synthesis and characterization of gold nanoparticles from the tetrachloroauric acid precursor by the citrate reduction method. Clusters of shiny dark spherical dots represent the GNPs in the TEM micrograph.

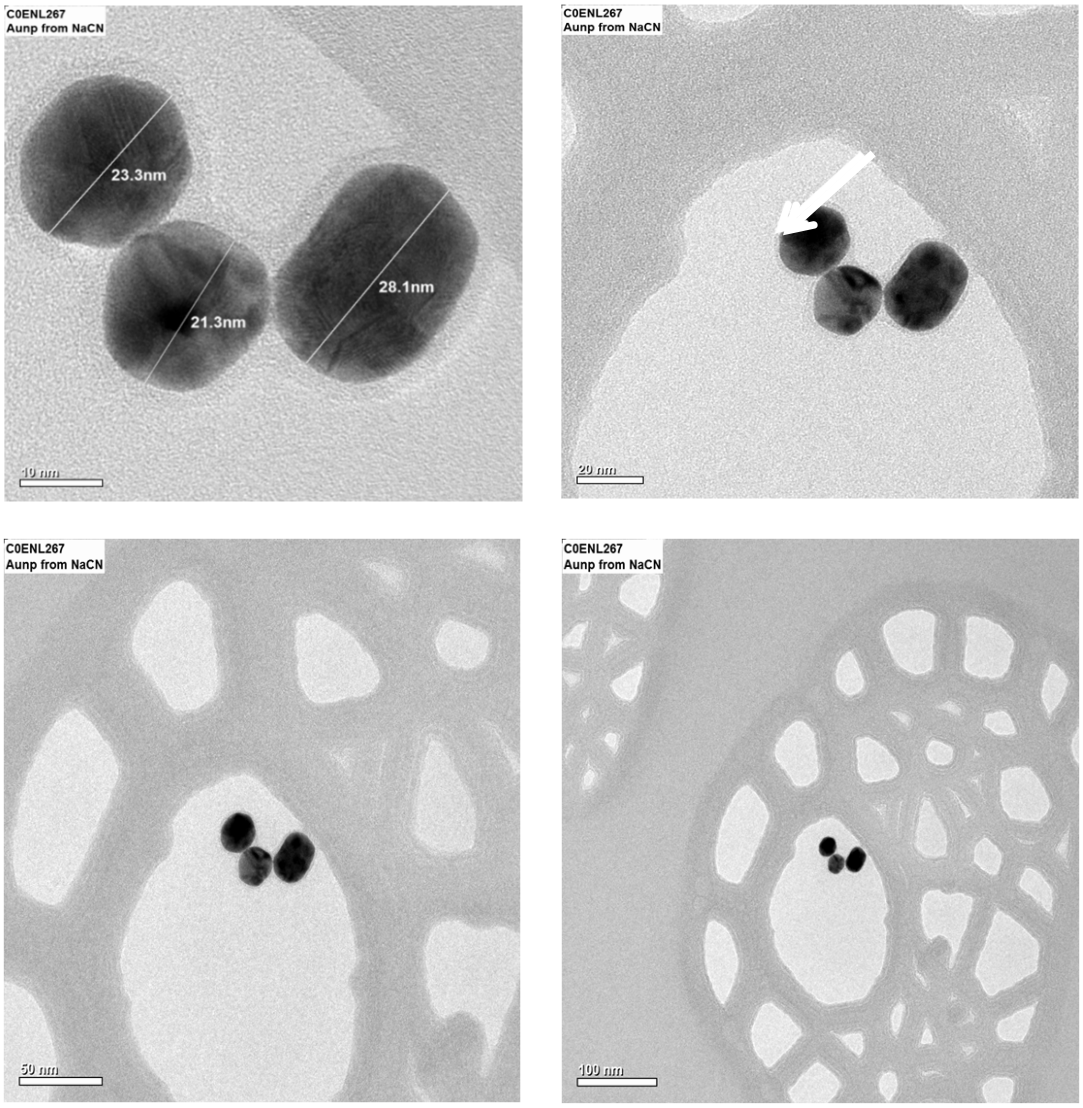


Plate 1. TEM image of synthesized gold nanoparticles from gold precipitated using sodium cyanide analar grade

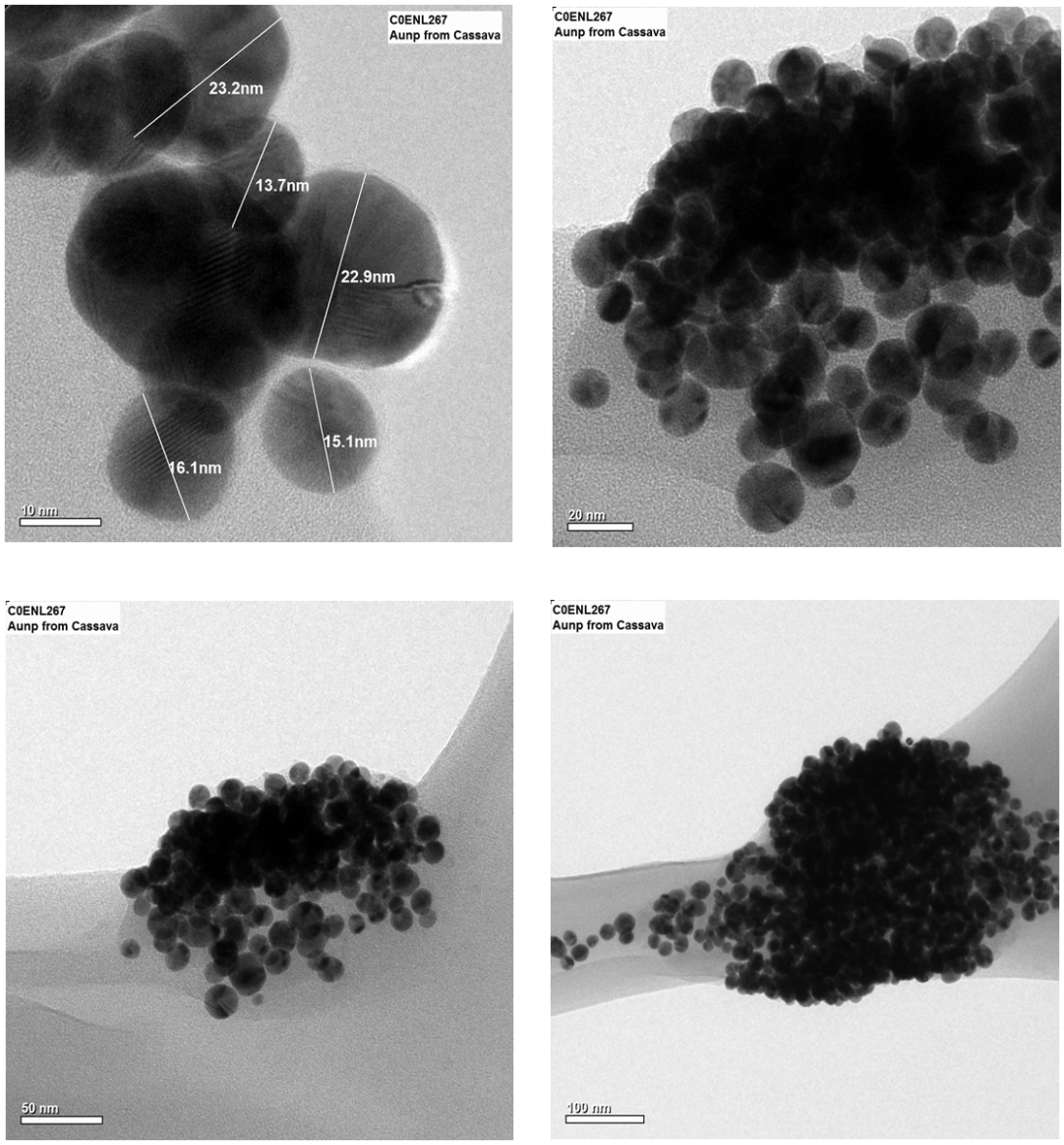


Plate 2. TEM image of synthesized gold nanoparticles from gold precipitated using cyanide solution from cassava

The structural characterization of the gold nanoparticles was evaluated using the x-ray diffraction (XRD). Fig. 3 shows the X-Ray Diffraction (XRD) pattern of the gold nanoparticles synthesized by chemical method. It can be observed from the XRD that the gold nanoparticles synthesized showed sharp and distinct diffraction peaks to confirm its crystallinity. The XRD pattern obtained corresponding to the gold nanoparticles exhibits Bragg reflections, which could be well manifested on the basis of the face centered cubic (fcc) gold nanostructures. The strongest diffraction peak at 38 degrees is considered to be of {1 1 1} facet of the face centered cubic structure (Fig. 1), while the diffraction peaks of other gold peaks at {2 0 0}, {2 2 0}, {3 1 1}, {2 2 2}, {4 0 0} and {3 1 1} are found to be much weaker compared to standard GNPs. At this miller index of {1 1 1}, the atoms orientation of the gold are at parallel intersection and the peak produced is the strongest. This is in agreement with the work of [35] that reported the facile biosynthesis of gold nanoparticles exploiting optimum pH and temperature of fresh

water algae *Chlorella pyrenoidusa.* The peak positions at 2θ = 38°, 44.52°, 65°, 77°, 82°, 98° and 111° represent the presence of gold nanoparticles which are in agreement with the Bragg's reflection of 2θ and the values are consistent. The XRD patterns clearly show that the gold nanoparticles are in crystalline in nature. The broadening of peaks in the XRD patterns was attributed to particle size effects. This is similar to the work of [36].

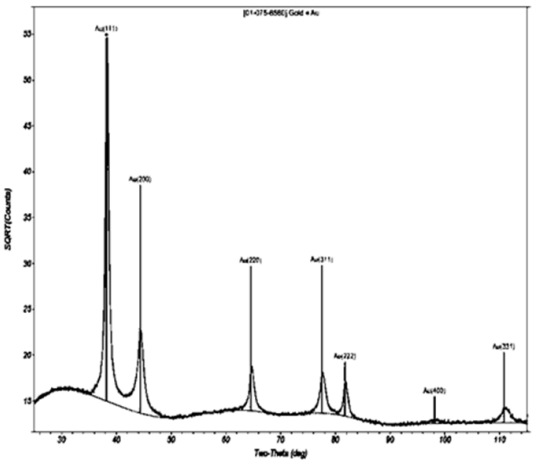


Fig. 3. X-ray diffraction (XRD) patterns of the gold nanoparticles synthesized by chemical method from precipitated gold using NaCN and cyanide solution from cassava

4. CONCLUSION

The TEM images have confirmed that high quality spherical gold nanoparticles in the size range between 18 nm – 24 nm have been successfully synthesized. The XRD shows that the material of the gold nanoparticles is gold and crystalline in structure. Narrow size distribution and small monosize gold nanoparticles produced may proffer advantages for self-assembled monolayer formation and enhanced surface area.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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