

Original Research Article**LABORATORY PREPARATION OF THE PRECURSOR FOR SYNTHESIS OF****GOLD NANOPARTICLES****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

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 [6]. 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. Three different gold concentrations gave different particle size distribution curves [24]. In another study, the monodisperse nanogold with different particle sizes were obtained by the same procedure with different amounts of citrate [25].

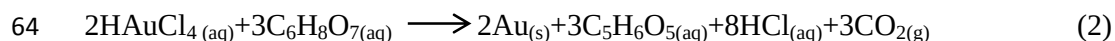
In the majority of the published citrate reduction works, it is interesting to note that the precursor used in the synthesis of GNPs is mostly sourced commercially. Information on the laboratory preparation of the precursor is very scanty or inaccessible in the literature. Hence, this work has presented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

EXPERIMENTAL

Gold nanoparticles [26] are usually synthesized by reduction reaction between analar grade hydrogen tetrachloroaurate (HAuCl_4) and trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$). 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 stirrer. 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 (HAuCl₄) solution. 0.5 mM HAuCl₄ was prepared in some distilled water and standardized. 50 ml of 0.5 mM HAuCl₄ was poured in a beaker and heated to boil on a hot plate with magnetic stirrer. 0.5 g of trisodium heptaoxocitrate (V) oxide (Na₃C₆H₅O₇) was dissolved in some distilled water and made up to mark in order to prepare 38.8 mM Na₃C₆H₅O₇. To this boiling solution, 5 ml of Na₃C₆H₅O₇ 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:



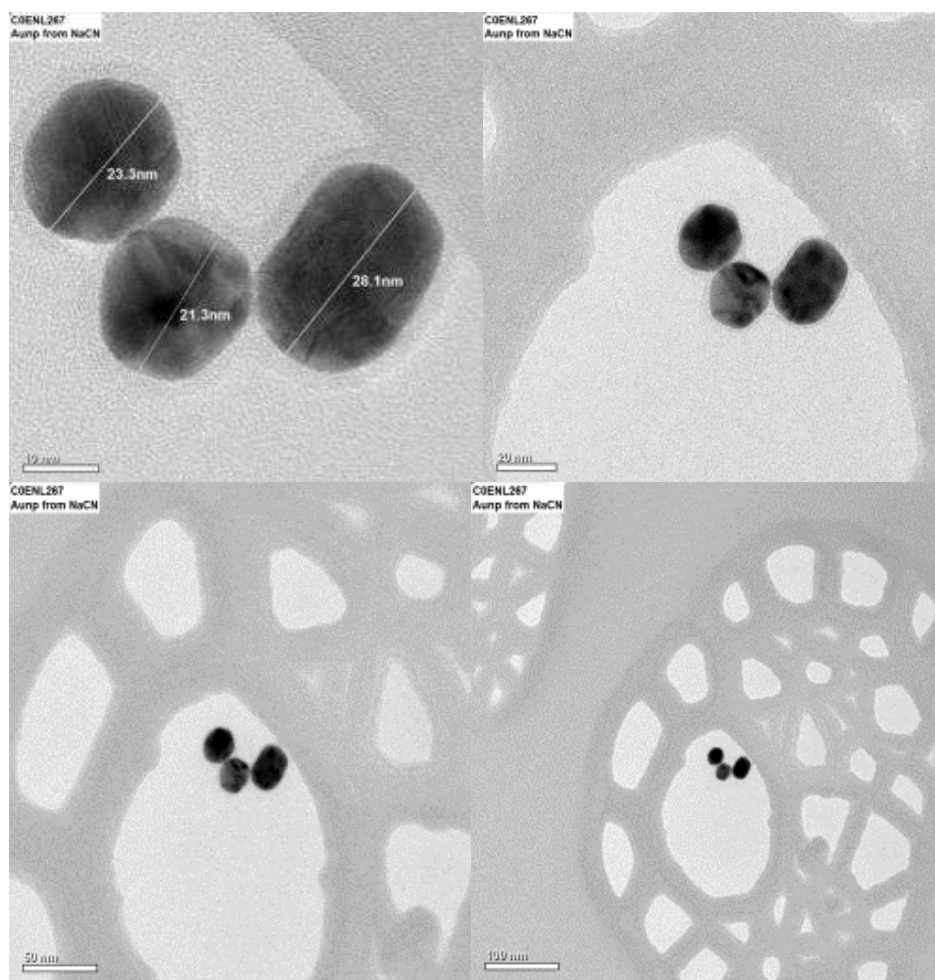
This solution was stored at 4°C for further use. The procedure above was repeated using gold precipitated from analar sodium cyanide.

RESULT 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 whole 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.

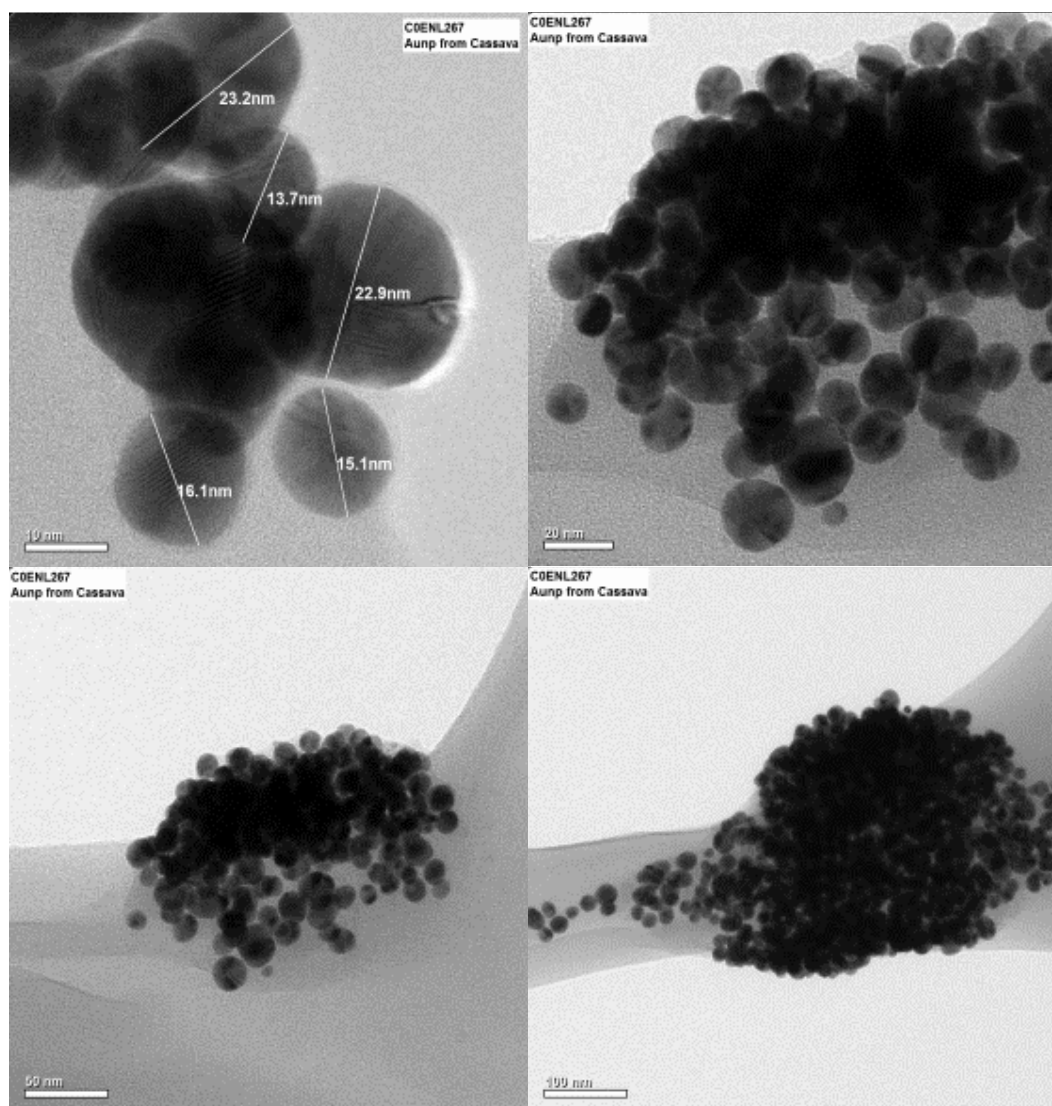
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Plate 1: TEM image of synthesized gold nanoparticles from gold precipitated using sodium cyanide analar grade

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(b)

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

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 whole 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 [26] who obtained 18 nm from synthesis and characterization of gold

94 nanoparticles from the tetrachloroauric acid precursor by the citrate reduction method.
 95 Clusters of shiny dark spherical dots represent the GNPs in the TEM micrograph.
 96 The structural characterization of the gold nanoparticles was evaluated using the x-ray
 97 diffraction (XRD). Figure 1 shows the X-Ray Diffraction (XRD) pattern of the gold
 98 nanoparticles synthesized by chemical method. It can be observed from the XRD that the
 99 gold nanoparticles synthesized showed sharp and distinct diffraction peaks to confirm its
 100 crystallinity. The XRD pattern obtained corresponding to the gold nanoparticles exhibits
 101 Bragg reflections, which could be well manifested on the basis of the face centered cubic
 102 (fcc) gold nanostructures. The strongest diffraction peak at 38 degrees is considered to be of
 103 {1 1 1} facet of the face centered cubic structure (Figure 1), while the diffraction peaks of
 104 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
 105 much weaker compared to standard GNPs. This is in agreement with the work of [26] that
 106 reported the facile biosynthesis of gold nanoparticles exploiting optimum pH and temperature
 107 of fresh water algae *Chlorella pyrenoidosa*. The peak positions at $2\theta = 38^\circ, 44.52^\circ, 65^\circ, 77^\circ,$
 108 $82^\circ, 98^\circ$ and 111° represent the presence of gold nanoparticles which are in agreement with
 109 the Bragg's reflection of 2θ and the values are consistent. The XRD patterns clearly show
 110 that the gold nanoparticles are in crystalline in nature. The broadening of peaks in the XRD
 111 patterns was attributed to particle size effects. This is similar to the work of [27]. X-ray
 112 diffraction measurements of the films and powders in the present studies were carried out
 113 using Rigaku automated x-ray diffractometer. The filtered copper K_α ($\lambda = 1.5418 \text{ \AA}$)
 114 radiation was used for recording the diffraction pattern.

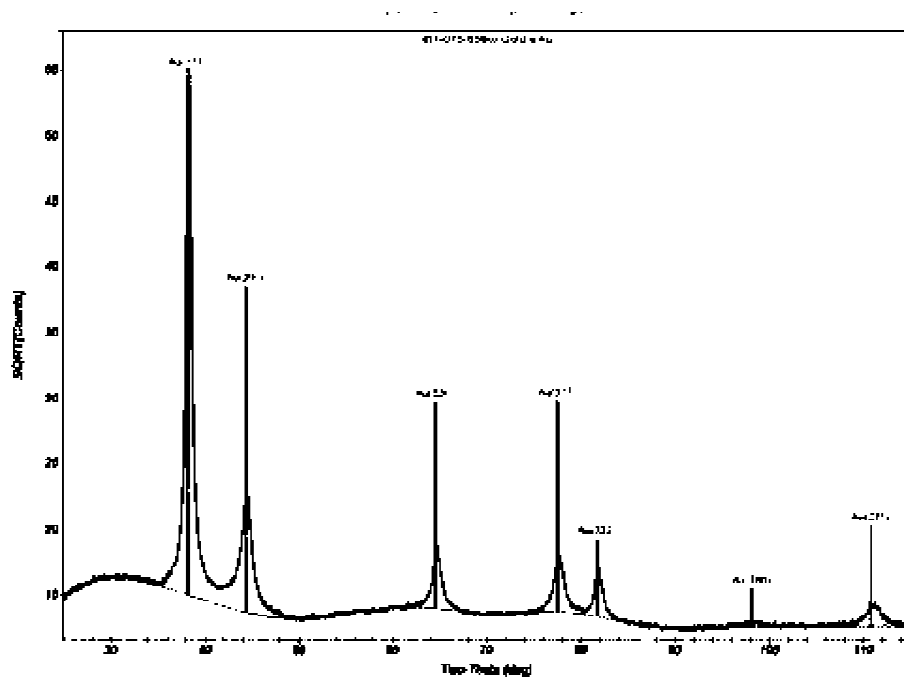


Figure 1 X-ray diffraction (XRD) patterns of the gold nanoparticles synthesized by chemical method from precipitated gold using NaCN and cyanide solution from cassava

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.

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