Comparative Study of Effect of Various Reducing Agents on Size and Shape of Gold Nanoparticles

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ABSTRACT

Gold nanoparticles are synthesized by reduction of gold ions by a reducing agent in the presence of a capping agent. Many properties (like electromagnetic, optical and catalytic) vary with size and shape of the nanoparticles. In this paper, a comparative study of the effect of various reducing agents on size and shapes of gold nanoparticles has been made. Gold nanoparticles formed by hydrazine sulphate as a reducing agent have branched or the so-called sea urchin shape resembling to the shape that of the familiar sea animal. This shape was synthesized for the first time. TEM images depicting the morphological and structural features of nanoparticles formed by different techniques have been shown along with some of their applications.

Keywords: Electromagnetic properties, Shape, Reducing agent, synthesize.

1 INTRODUCTION

Nanoparticles have attracted considerable interest because of their unique optical, electromagnetic and catalytic properties that differ from the bulk ones. The origin of these properties is their large surface to volume ratio and from the coherent oscillation of the conduction electrons that can be induced by interactive electromagnetic fields. Recently, gold nanoparticles have found their large application in medical technology. Gold nanoparticles are being used to deliver protein-based drugs, and are of particular utility because the particles can carry multiple active groups. For example, they can be designed with targeting groups that direct treatment to a particular cell type, and also carry pharmacologically active groups that exert a therapeutic effect. One of the keys to understanding the size-dependent properties and applications of nanoparticles is generating libraries of particles with diverse sizes for physical study. Since many properties vary with the size and shape of the novel metal particles, the focus of many studies has been on the methods for controlling the size and shape of gold nanoparticles. The aim of this work has been to compare the effect of various reducing agents on size and shape of gold nanoparticles formed.

2 EXPERIMENTAL

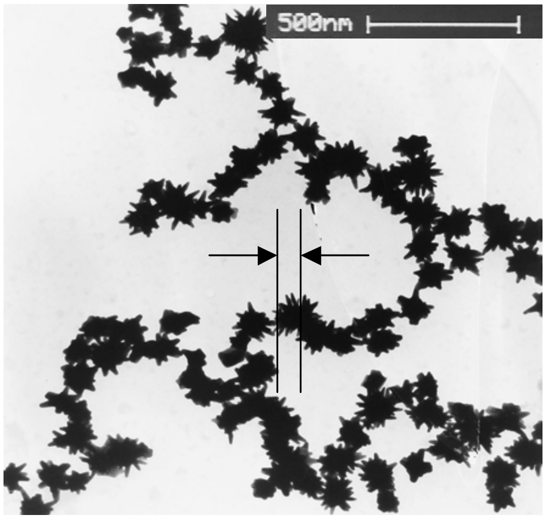
Five identical samples of gold ions were prepared as follows. In each of the five conical flasks, 500 μL of 0.01 M $HAuCl_4$ and 500 μL of 0.01 M sodium citrate were added to 19 mL, 18 Ω deionized water. Sodium citrate acts as a capping agent, which prevents agglomeration of gold nanoparticles when they are formed. Each of the gold ion solution was reduced in a different way using different reducing agents. 500 μL of 0.1 M freshly prepared hydrazine sulphate (Sample A), 500 μL of 0.1 M freshly prepared $NaBH_4$ (Sample B), 500 μL of 30% hydrogen peroxide (H_2O_2) (Sample C) and 500 μL of 0.1 M potassium ferrocynide (Sample D) were added to four different samples and shaked gently for 7-10 seconds till the color changed indicating nanoparticles formation. Sample E was prepared by addition of 500 μL of 0.1 M ascorbic acid and heating at 60°C for 20 minutes. In yet another experiment involving synthesis of gold nanoparticles, 1000 ppm $KAu(CN)_2$ was reduced by 0.1 M freshly prepared $NaBH_4$ (Sample F). Each of the samples was left undisturbed after which they were analyzed by transmission electron microscopy (TEM). 2-3 drops of each solution were placed on carbon-coated copper grids for a transmission electron micrographic examination.

3 RESULTS AND DISCUSSION

The morphology of gold nanoparticles along with their size and shape has been outlined in the form of a grid with a short description for each morphology type. The nanoparticles formed have large surface area and hence large surface energy associated with them. As a result, they tend to agglomerate in order to lower their surface area and attain stable state. Use of a capping agent like sodium citrate is thus essential to prevent immediate agglomeration. The gold nanoparticles synthesized with the help of various reducing agents were characterized by TEM within 1 hr. of their synthesis so as to achieve non-agglomerated morphology of gold nanoshapes.

4 GOLD NANOPARTICLES GRID

A.



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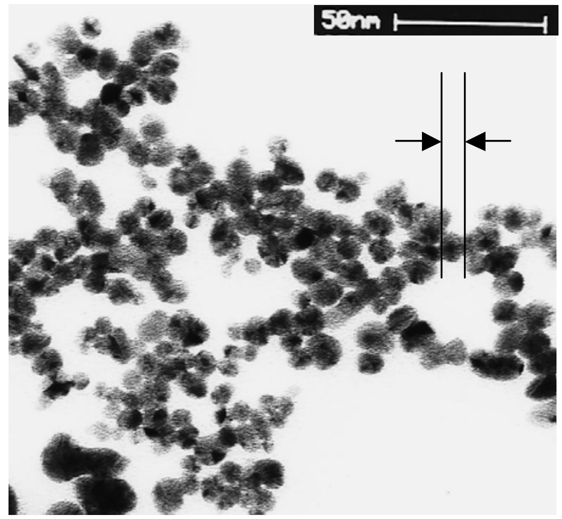


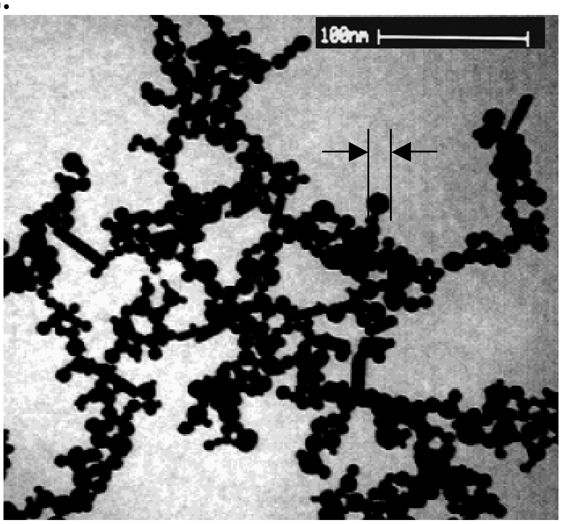
Reducing Agent: Hydrazine sulphate
Shape: Sea urchin
Size: 100-125 nm

Gold nanoparticles formed by this technique have approximately 18-20 needles erupting from a central core of 100-125 nm size nanoparticle. The length of longest needle observed is 70 nm and that the shortest needle is 10 nm long. The general aspect ratio of needles is 4:1. Such needles are assumed to be formed due to the ongoing competition between the hydrazine and the sulphate group towards the gold ion to be reduced, gold particles being attracted by sulphate group to some extent. These nanoparticles may act as active seeds for branched nanorods and nanowires synthesis.

Reducing Agent: Sodium borohydride
Shape: Nearly spherical
Size: 5-7 nm

Sodium borohydride being one of the strongest reducing agent reduces gold ions at the very instant it is put into solution containing gold ions and capping agent. Hence 5-7 nm size nanoparticles are synthesized. Citrate ions act as capping agents and prevents agglomeration upto certain extent. Within 5 hours of preparation the pink color of solution disappears indicating agglomeration of gold nanoparticles. These spherical gold nanoparticles are used as seeds to synthesis variable aspect ratio nanorods in the presence of a directing agent. The nanoparticles together with nanorods are used to detect various cancers and ulcers in human body.

C.



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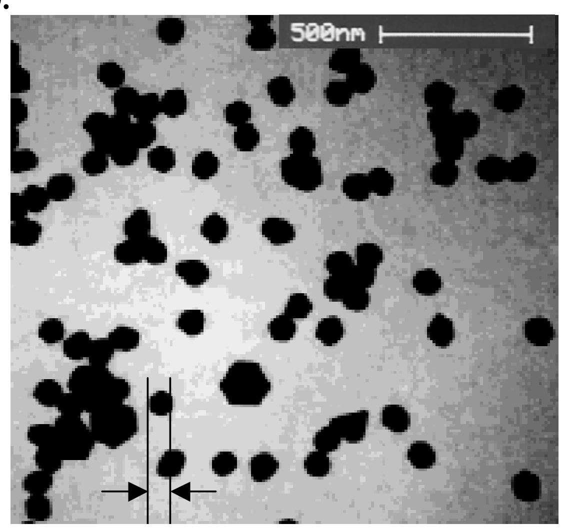


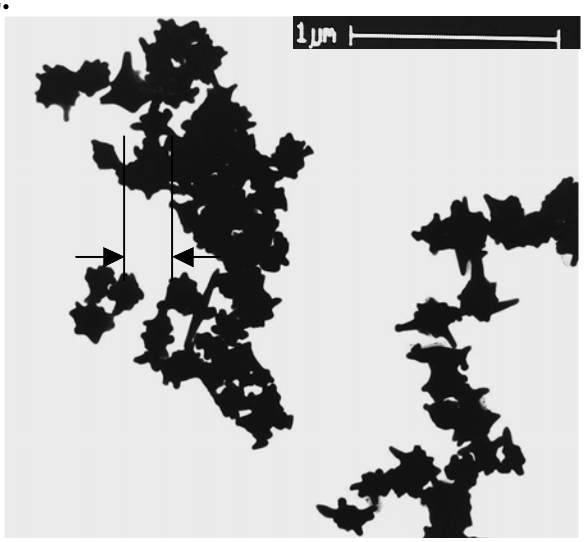
Reducing Agent: 30% Hydrogen peroxide
Shape: Spherical
Size: 5 nm

Synthesis of gold nanoparticles by using hydrogen peroxide showed smallest nanospheres (size: 5 nm) among all reducing agents used. There were also some large nanospheres of size range 15-20 nm. Apart from spherical structures nanorods upto length 50 nm and diameter 5 nm (aspect ratio = 8:1) were also observed. Hydrogen peroxide is a strong bleaching agent and can reduce gold ions very effectively. Nanospheres of this size range are best suited for biomedical applications. The exact reason behind the formation of nanorods is not known since no directing agent or micellar template was used.

Reducing Agent: Potassium Ferrocynide
Shape: Spherical nanospheres and plates
Size: 65-75 nm

Comparatively large nanoparticles of gold are produced using potassium ferrocynide as reducing agent. Potassium ferrocynide being weak reducing agent reduces gold ions slowly as compared to that reduced by sodium borohydride and hydrogen peroxide. Hence gold particles have more time to increase their size. Apart from nanospheres again some nanoplates are seen the exact reason behind formation of which is still to be known. Plates having 4 and 6 sides are easily seen. The length of each side of nanoplate is approximately 60 nm. The solution color changes to bluish-pink indicating nanoparticle formation. Blue color is due to use of potassium ferrocynide as reducing agent.

E.



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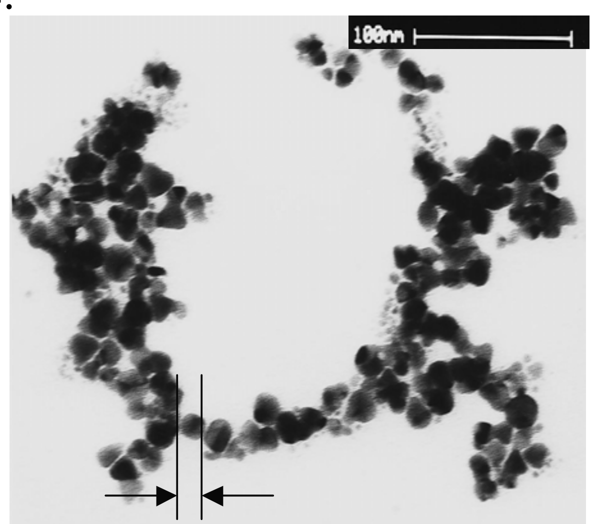

Reducing Agent: Ascorbic acid
Shape: Distorted shaped along with needles
Size: 200-225 nm

Ascorbic acid is a weak reducing agent and cannot reduce gold ion at room temperature or without any surfactant. Hence reduction was carried out at 60°C for about 20 min. The shape of gold nanoparticles is distorted with general size range 200-225 nm. These nanoparticles formed have high tendency to agglomerate and hence reduce surface energy to attain stable state. The exact mechanism and nature of formation of these nanoparticles by ascorbic acid reduction is yet to be understood. Due to their large size, these may also be termed as "pseudo gold nanoparticles". Some long needles of aspect ratio upto 10:1 were also observed.

Reducing Agent: Sodium borohydride (Reduction of gold cyanide ions)
Shape: Spherical
Size: 10-15 nm

For comparing relative affinities of chloride and cyanide ligands with gold core, an attempt to reduce gold cyanide ions with sodium borohydride was made. 1000-ppm solution of gold cyanide ions when reduced by 0.1 M borohydride solution (freshly prepared) gave gold nanoparticles, which were of size range 10-15 nm (bigger than those synthesized from gold chloride ions under same set of conditions). It may be assumed that cyanide has larger affinity with gold atom as compared to chloride. Moreover, large ranges of nanoparticles were found to be synthesized.

5 APPLICATIONS

Gold has attracted much attention in catalyst research and industrial applications. It has been demonstrated that gold nanoparticles (5-8 nm) dispersed on metal oxides can exhibit high catalytic activities for various types of reactions, like the epoxidation of propene and the low temperature oxidation of CO. The use of carbon nanotubes as potential catalyst supports is now attracting the interest of the catalytic community with evidence of unique metal/support interactions resulting in quite distinct catalytic behavior [4].

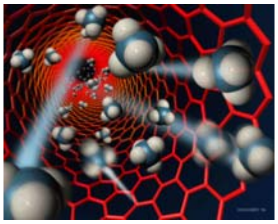

Figure 1: Au nanoparticles homogeneously dispersed on the surfaces of the CNTs.

These are also very good at scattering and absorbing light and this property is harnessed in a living cell to make cancer detection easier (Figure 2). Gold nanoparticles have 600 percent greater affinity for cancer cells than for non-cancerous cells [5]. Gold nanoparticles have also found applications in the field of electronics like digital data storage that requires them to form ordered arrays (Figure 3).

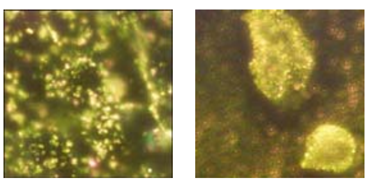

Figure 2: Binding gold nanoparticles (35-50 nm) to a specific antibody for cancer cells makes cancer detection easier.

6 CONCLUSION

Tiny billionth-of-a-meter sized clusters of gold atoms - gold "nanoparticles" — are being widely studied by scientists. They have many useful potential applications, from carriers for cancer-treatment drugs to digital data storage. We have provided a comparative study, in the form of a table for better understanding, of the effect of various reducing agents on the size and shapes of gold nanoparticles. Gold nanoparticles formed by hydrazine sulphate as a reducing agent have branched or the so-called sea urchin shape resembling to the shape that of familiar sea animal. This shape was synthesized for the first time and may find applications in various biomedical or related fields. The exact mechanism and nature of these branched gold nanoparticles is still under scrutiny at our research laboratory and full effort is being made to control the aspect ratio of needles erupting from the central core along with control in core size.

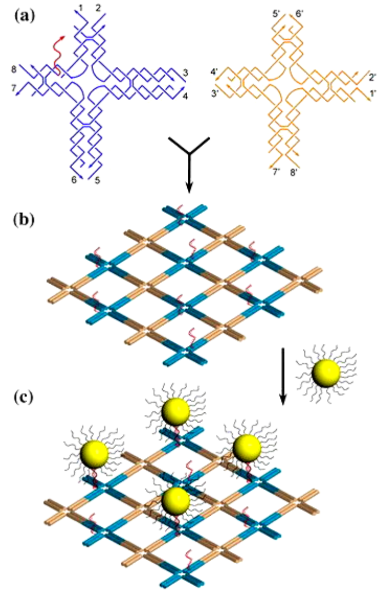

Figure 3: (a) Two-tile system of nanogrids; (b) DNA nanogrid (c) Ordered gold nanoparticles (~100 nm) on DNA grid [6].

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