Mechanism of gold nanoparticle formation by reduction from aqueous solutions

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Abstract

Research on gold nanoparticles (GNPs) has been boosted by a wide variety of potential applications, such as electrochemistry, catalysis, medicine and nanodevices. The aqueous solutions reduction method for the synthesis of GNPs has known advantages but normally provides products with low nanoparticle concentration, wide size distribution and unregulated morphology.

Special attention is given in this paper to the formation of GNPs using sodium citrate as a reducing agent from aqueous solutions. The aim was the improved control of the synthesis process of GNPs and GNPs resulting in more homogeneous sizes and morphologies. The synthesis of GNPs was investigated changing the reaction parameters (e.g. the concentration of reduction agent and the reaction temperature).

The morphological and structural characterization of GNPs investigated by TEM and chemical analysis were presented. GNPs produced in the same research group in Aachen by hydrogen reduction of a chloroauric acid $HAuCl_4$ aerosol using ultrasonic spray pyrolysis method are used as a benchmark for further applications.

1 Introduction

Gold nanoparticles(GNPs), have attracted increasing attention due to their unique properties in multidisciplinary research fields. They are available with diameters ranging from a few to hundreds of nanometres. Remarkably, novel emerging applications bring a huge growth of the global demand for GNPs. For example, GNPs are used largely as bio delivery vehicles in medicine [1]. GNPs are developed as catalysts in new usages [2]. To meet the enlarging demand for GNPs, more attention should be paid to effective synthesis methods, which should also be environmentally friendly and energy saving.

From our previous work [3, 4], GNPs were synthesized by Ultrasonic Spray Pyrolysis (USP). The results suggest that USP enables the synthesis of pure GNPs with a size of hundred nanometres. To supplement the size control, our aim was to produce pure GNPs ranged from 10nm to 100 nm by

reduction from aqueous solution using sodium citrate in order to study this process for the subsequent synthesis of monometallic and bimetallic catalysts (Au/TiO_2).

2 Experimental Part

Materials

Trisodium citrate (Alfa Aesar, 99.999%), $HAuCl_4 \cdot 3H_2O$ (Alfa Asear, 99,0 %min), Dialysis membrane(Spectrum Laboratories, Inc.), Ultrapure deionized water was used for all solution preparations. All glassware was cleaned with aqua regia.

Synthesis of GNPs via different $Na_3C_6H_5O_7$/Au ratios:

GNPs were synthesised by the water bathed citrate reduction method, through the chemical reduction as described by Turkevich and Frens [5, 6]. We set up easy reaction equipment like sets of beakers, which is more convenient and possible to obtain uniform temperature distribution.

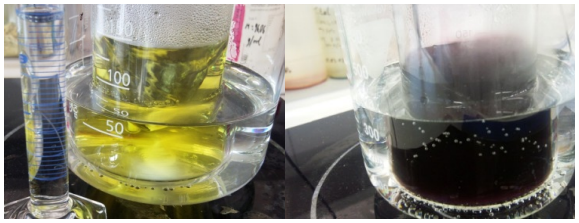

Figure 1: Water bath citrate reduction of gold nanoparticles

GNPs were synthesized from a 10mg Au in 100ml $HAuCl_4$ aqueous solution increasing the volume of 1% trisodium citrate solution. In detail, 0.5ml, 1ml, 1.5ml, 2ml, 2.5ml of 1% trisodium citrate solution were preheated and added quickly into the $HAuCl_4$ solution while stirring and heating for 15min, then kept stirring until the nanogold solution cooled down.

Synthesis of GNPs with increasing Au concentration

A series of 100ml aqueous solutions containing different Au concentration, 10mg, 25mg, 50mg, 75mg, 100mg, were prepared. Using the same water based method, we then added a preheated relative volume of 1% trisodium citrate solution with the same $Na_3C_6H_5O_7$/Au ratio as 3.4.

Synthesis of GNPs under higher temperature and pressure

10mg Au/100ml $HAuCl_4$ aqueous solution and 1ml 1% $Na_3C_6H_5O_7$ were prepared. We use the autoclave to make the reaction temperature at 150^{o}C (about 0.5 MPa), 2h, and sampling 5 times during this procedure.

GNPs Purification

To obtain purified nanogold solutions by reduction from trisodium citrate, we purified our samples by the dialysis method.

Used measurements for the particle analysis

A Transmission Electron Microscope JEOL JEM-2100(HR) with attached Energy Dispersive X-ray Spectrometer EDS (JEOL JED-2300 Series) was used at the Faculty of Mechanical Engineering in Slovenia.

3 Results and discussion

Sample 1 with 10mg Au/100ml $HAuCl_4$ aqueous solution and 1ml 1% $Na_3C_6H_5O_7$, water based method dialysis experiment for 48h has been characterized by chemical analysis and TEM. The chemical analysis results indicated, after dialysis the concentration of Na^+ is less than 1ppm and Cl^- is 16mg/L. This result demonstrated here experimentally that gold nanoparticles solution can be purified using the dialysis method. Consider about the concentration changes of Cl^-, from 95mg/L to 16mg/L, dialysis duration should be longer than 48h to get more purity gold solutions. Fig. 2 shows the TEM images of Sample 1, and these GNPs size distribution range from 10nm to 50nm, were measured from TEM images. The morphologies of these GNPs were inhomogeneous.

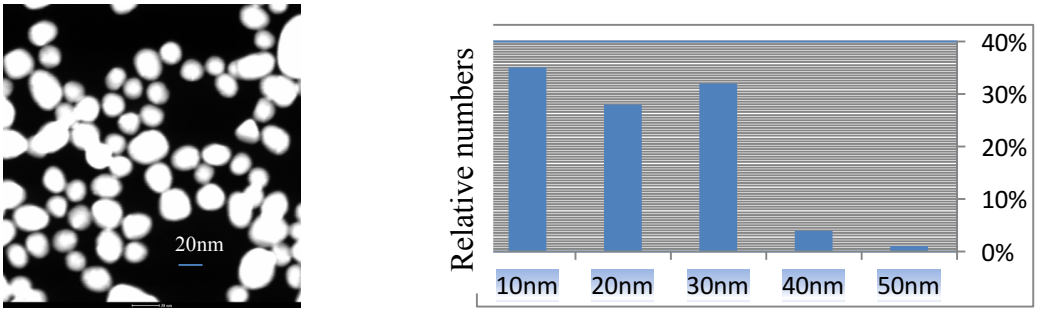

Figure 2: TEM images and distribution diagrams of GNPs for Sample 1

For further purification we prepared Sample 2 and Sample 3 with 10mg Au/100ml $HAuCl_4$ aqueous solution while 0.5ml and 2.5ml 1% $Na_3C_6H_5O_7$, water based method, dialysis experiment for 144h, which were then characterized by chemical analysis and TEM. From Table 1 it was found that dialysis for 144h could obtain purified nanogold solutions by reduction from trisodium citrate, and that a relatively large volume of trisodium citrate will help obtain GNPs with smaller size, which is indicated in Fig. 3(a). These findings are consistent with the results of Frens [6].

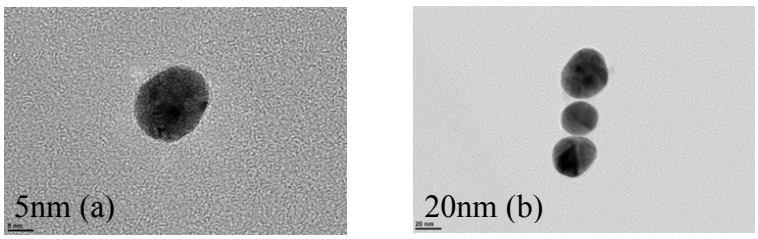

Figure 3: TEM images for (a) Sample 3, reacted at boiling point, 15min; (b) samples 4, reaction temperature 150°C, 2h

Table 1: Chemical analysis results for Sample 2, Sample 3 dialysis for 144 h

Samples	Au	Na	Cl
	ppm	ppm	mg/L
Sample 2 (before dialysis)	100	53	90.6
Sample 3 (before dialysis)	113	296	10.8
Sample 2 (dialysis 144h)	94	7	0.94
Sample 3 (dialysis 144h)	81	6	0.04

A higher temperature experiment with 10mg Au/100ml $HAuCl_4$ aqueous solution and 1ml 1% $Na_3C_6H_5O_7$ reacted at 150°C for 2h to form the ruby-red colour solution. Fig. 3(b) is the TEM images for a higher temperature sample after dialysis for 144h. Contrast to sample reacted at boiling point, 150°C reaction need much more time and result in smaller particles with lower size distribution and more homogeneous morphologies.

4 Conclusion

In this work, purified spherical GNPs with smaller size, between 10nm to 50nm can be obtained from the chloroauric acid precursor by the citrate reduction method via normal boiling temperature and higher temperature at 150°C. And the results reveal at 150°C, we can get GNPs relatively homogeneous with an average diameter of 10nm, while this procedure needs much more time than reduction reactions at boiling point.

Dialysis nanogold solutions for 144h could obtain purity nanogold solutions by reduction from trisodium citrate.

From the experiment with increasing concentration of Au in $HAuCl_4$ aqueous solution, we found that the increasing Au concentration obviously increase the reduction duration.

The modified double beaker system and autoclave higher temperature reactor for citrate reduction can produce GNPs with lower size distribution and more easy to handle on a large scale, in order to meet huge industrial demand.

The full paper will be published soon after the conference in a scientific journal.

5 References

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