SYNTHESIS OF GOLD NANOPARTICLES VIA CHEMICAL REDUCTION METHODS

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Abstract

Gold nanoparticles are currently experiencing an exposion of researches of their properties and their application potentials. The development to the next generation of nanotechnology reqiures products of gold nanoparticles having preciesly controlled size, shape, purity, and large production fecility.

Up to now it has not been yet possible to produce gold nanoparticles in large scale for industrial productuion. Such the present investigation aims an efficient and convienient production routes to generate spherical and purified gold nanoparticles. The main tagets are to generate uniform gold nanoparticles in aquous solutions via chemical reduction methods, and to modify the production routes for their industrial production which could generate final products in good quality and large quantity.

Here we present the citrate reduction process and the $NaBH_4$ reduction process in aqueous solutions, and both of these processes were scaled up. Different experimental parameters have been studied to optimize the process. Dialysis are applied as the post treatment for gold nanoparticles in aqueous solutions to achieve high drgree purity, together with the study of the stability of gold nanoparticles.
Nanotrac Wave analyzer, TEM and ICP analysis methods are used in the study to measure the particle size distribution, and the purification degree of the gold nanoparticles.

Keywords: Gold nanoparticles, citrate reduction process, NaBH4 reduction process, purification

1. INTRODUCTION

Nanotechnology has emerged in the last decades, which is developed with high speed and is now undergoing a revolutionary. There is no doubt to say nanotechnology is preparing to play a significant and commercial role in our future society [1]. Gold nanoparticle is the most stable metal nanoparticles, and they present fascinating aspects such as their size-related electronic, magnetic and optical properties, biocompatible, non-cytotoxic properties, their assembly of multiple types, surface functionalization, and their applications to catalysis and biology [2]. All these promise gold nanoparticles an important building block. By now the global market for gold nanoparticles is still in its infancy, although it can be foresee that a rapid development would show up in the next few years [3], we still lack the ability to deliver large amount of gold nanoparticles with stable good quality. There are certain short boards for the existence synthesis processes of gold nanoparticles. Therefore an efficient, stable and convenient process for the production of gold nanoparticles is of importance. The development of a complete production route is challenge.

Various syntheses of gold nanoparticles were reported and reviewed. The Turkevich method, also named the Citrate reduction method is one of the most classic processes. It is popular and convenient, however the products' stability and dispersity are often limited. In recent years, this synthesis was developed to control the process by adjusting the reaction conditions to presents improved results with higher monodispersity and a better size control [4, 5]. Through these investigations, we know these solutions are sensitive to the changes in PH, the ionic strength of the medium, and the presence of other organic materials, and this promoted the Turkevich process to be controllable with certain defined size distribution requirments. Therefore the Turkevich process is considered as a promising method to be developed as a suitable route for the quantity production of spherical gold nanoparticles.

To innovate the Citrate reduction method, and conquer the short boards specially the broad size distribution, additional reductant Sodium borohydride ($NaBH_4$) have been chosen and studied in this paper, and the new process use $NaBH_4$ as a reductant was then defined as the $NaBH_4$ reduction method.

$NaBH_4$ is well known as the main reductant for the classic Brust process, which involved a biphasic methods requiring phase transfer reagents are valued for obtaining high quality materials with narrow size distributions, while simple single phase methods often fail to yield products of equal quality. There is no doubt to say the Brust process of gold nanoparticle synthesis is a valuable technique for preparing thiol-stabilized nanoparticles, but the functional groups are limited by the compatibility of thiols, the identification of a unique set of reaction conditions is often required for the preparation of each functionalized target, and most of the method in these reports are always accompanied with hazardous synthesis process [6].

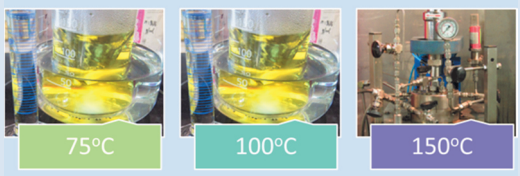
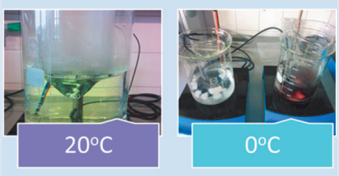
In the ideal synthesis process, precisely control over the particles' size, shape, dispersity, and purity at the same time are required. Furthermore, industrial production of gold nanoparticles is aimed to be synthesized in an efficient, continuous process, resulting in reduced waste, high production yield and increased control of products properties. Therefore, several modifications should be design to modify the current synthesis process.

To improve the quantity of the final production of gold nanoparticles, a proper post treatment is necessary. The current purification processes are not usually effective to remove all the impurities, and few of them reported the method with detailed results [7]. Study of the efficiency for the purification process is very important for gold nanoparticles' commercial production.

2. EXPERIMENTS

Gold nanoparticles are synthesized by the citrate reduction method and the $NaBH_4$ reduction method in this article. To get a better control over the synthesis process, and the large-scale production of citrate stabilized gold nanoparticles, different experimental parameters are studied. To facilitate further applications, dialysis was applied as the post treatments to purify citrate stabilized gold nanoparticles.

Table 1 Gold nanoparticles synthesized via the citrate reduction method and the $NaBH_4$ reduction method with detailed experimental parameters

Mehtods / Key parameters	Citrate reduction Method	$NaBH_4$ reduction Method
Concentration of reductant (mg/100ml)	5 10 15 20 25 — Group Citrate 1 4 8 12 16 20 24 28 32 36 40 — Group Citrate 2 Au : 10mg Au/100ml	372.6 74.5 7.45
Concentration of precursor (mg Au /100ml $HAuCl_4$)	$Na_3C_6H_5O_7$/Au molar ratios of 0.68 10 25 50 75 100 — Group Au 1 5 10 20 40 — Group Au 2 $Na_3C_6H_5O_7$/Au molar ratios of 2.45	125 12.5
Reaction conditions		

Chemical and instrument used: hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$) ACS, 99.99% and trisodium citrate dehydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) 99% were purchased from Alfa Aesar GmbH & Co KG. Sodium

borohydride ($NaBH_4$) was purchased from AppliChem GmbH. The dialysis membrane is standard regenerated cellulose membrane: Spectra/Por 3 3.5kDa, purchased from Spectrum. Ultra-purified water (18.2 MΩ cm, Millipore) was used in all experiments.

2.1. The citrate reduction process

The reduction of a tetrachloroauric acid ($HAuCl_4$) has been initiated by trisodium citrate ($Na_3C_6H_5O_7$) by injecting specified amount of preheated trisodium citrate solution to a boiled gold solution in a double walled reactor, which is heated by a bath thermostat in order to prevent the presence of temperature gradients in the liquid. We set up easy reaction equipment like sets of beakers, and this mantel assured a homogeneous temperature distribution within the reaction solution. A temperature controller is used to control the water bath temperature. The mixture liquid was vigorously stirred by Teflon coated magnetic bars. The color of the solution changed gradually from transparent light yellow, dark black, and finally to the characteristic wine-red, which indicated the formation of gold nanoparticles. The heating mantle was removed after 20 min. The amounts of tetrachloroauric acid and trisodium citrate were varied to achieve different particle size distributions. After a defined time, the liquid was cooled to room temperature and purified by post treatment. During the synthesis process, all the glass wares used in the experiments are deep cleaned by aqua regia.

2.2. The $NaBH_4$ reduction process

In the $NaBH_4$ reduction process, $NaBH_4$ is the reduction agent and the citrate acted only as a stabilizing agent. The reaction rate in this single aqueous system was controlled by the reaction conditions. Different reaction parameters (e.g. reaction temperature, reactant concentration, addition rate for $NaBH_4$) were studied to get gold nanoparticles with uniform size distribution.

The experiment with optimized reaction parameters was performed as below: $NaBH_4$ solution with the concentration of 0.02mol/l was freshly prepared using ice cold water. The double beaker experiment mantel was filled in with a mixture of ice and water to maintain the reaction temperature at freezing point. First 3.94ml $HAuCl_4$ 1.25g Au /L aqueous solution was 10 times diluted, then 1ml 1% $Na_3C_6H_5O_7$ solution was added and mixed with the ice cold $HAuCl_4$ solution, the mixture liquid was vigorously stirred by Teflon coated magnetic bars. 3.94ml 0.02mol/l $NaBH_4$ solution was 10 times diluted by ice cold water, and then be added drop by drop into the ice cold mixture, which would take about 3 minutes to complete. The color of the mixture solution immediately presented pink. Continue stirring the solution for another 15 minutes. The color of the solution finally tuned wine-red. The acquired samples were stored in brown shading bottle and kept in cool environment at 4°C. The process is scaled up to 1L.

2.3. The post treatment

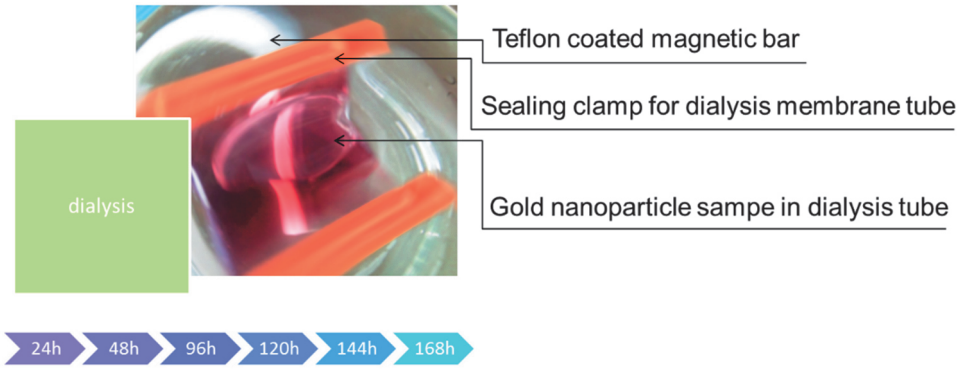


Fig. 1 Scheme purification processes for gold nanoparticles in this study

Dialysis: About 50ml gold nanoparticle solution was used in each dialysis set. The volume of ultra-purified water used in the process is 40 times volume of gold nanoparticle samples. To study the dialysis performance

according to the detention time, a process of 7 days was planned. Each identical sample was dialyzed under the same experimental condition for different detention time, from 24h to 168h. The water was refreshed every 24h. The dialysis process was performed at room temperature under shade.

2.4. Characterization

After the synthesis process, gold nanoparticle samples are characterized by TEM, Nanotrac wave analyzer, and ICP measurements. Nanotrac Wave Analyzer can provide particle size analysis by using the Microtrac FLEX application software program. Three main values are acquired for each measurement: MV-Mean Value Diameter, MN-Mean Number Diameter, MA-Mean Area Diameter.

3. RESULTS AND DISCUSSION

3.1. The citrate reduction method

In experiments, the concentrations of citrate and Au in solutions, and the reaction temperatures are studied. Synthesis processes are performed under higher and lower temperatures, 150°C and 75°C, and the longer reaction duration for both indicated that reaction at 100°C could speed up the reaction process.

Fig. 2 shows that when the ratio of initial concentration of citrate to gold is varied from 0.27 to 2.72, the final mean diameter of the particles formed varies, while subsequent increases in the ratio hardly have any effect on the size. Compare the reaction temperature from100°C to 75°C, a narrower particle size distribution and uniform morphologies is access at 100°C. Results also suggested the interplay of these parameters, theirs roles affected with each other. The influence of the temperature is affected by the citrate concentration, when the citrate concentration is high enough, the lower reaction temperature influence could be minimum.

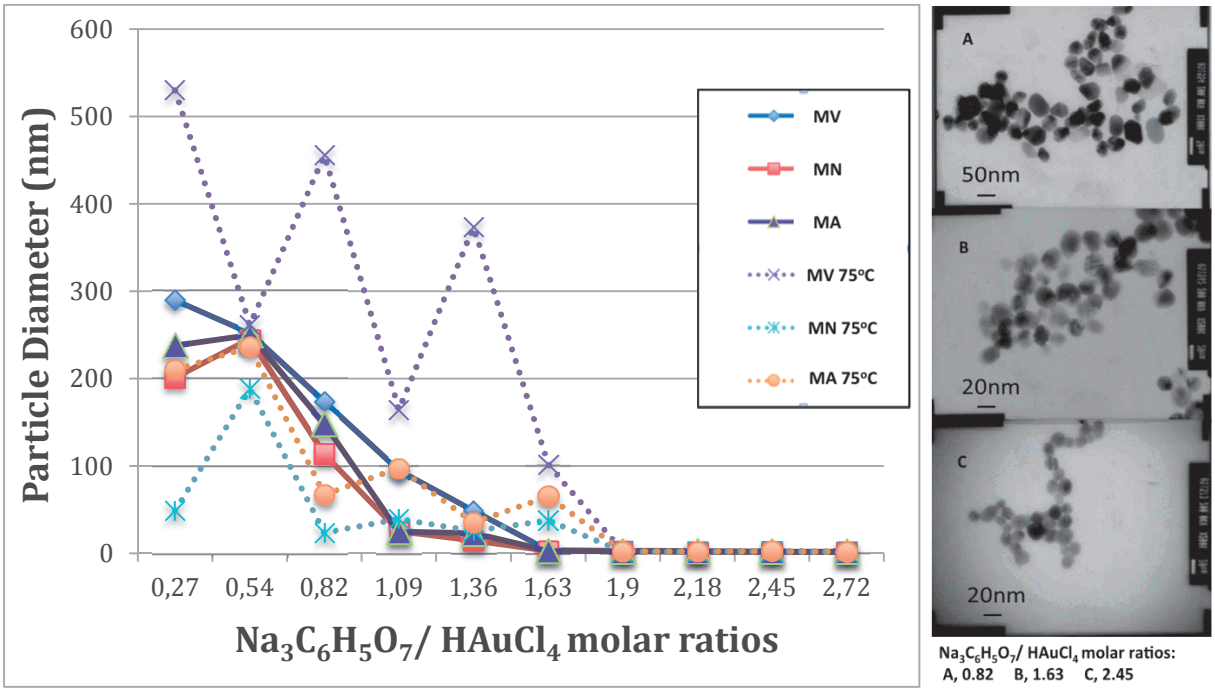


Fig. 2 Average particle diameter changes and different morphologies for gold nanoparticles with different $Na_3C_6H_5O_7$/Au molar ratios via citrate reduction method (**right:** particles mean diameters evaluated by Nanotrac wave analyser, **left:** TEM images of the synthesized gold nanoparticles)

Fig. 3 indicated the influence of Au concentration to the final particle size distribution evaluated by Nanotrac wave analyzer and TEM, it can be seen that higher Au concentration leads to a broadening of the gold nanoparticles' size distribution, and formed large and irregular gold nanoparticles. When the concentration is higher than 40mg Au per 100ml, the gold nanoparticles suffered a severe aggregation.

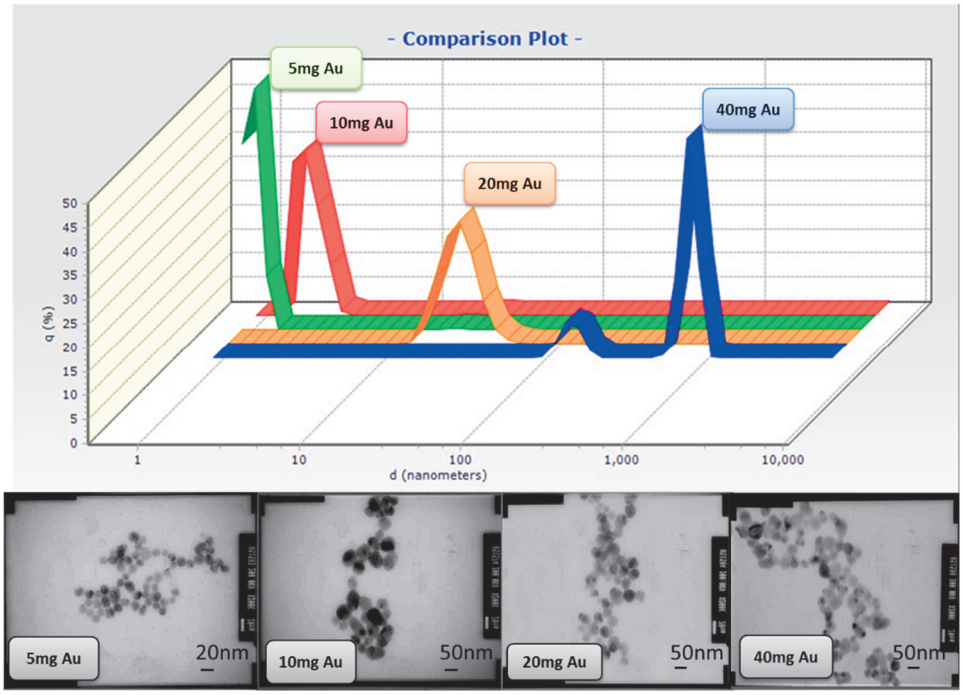


Fig. 3 Particle size distribution and different morphologies for gold nanoparticles via citrate reduction method with different Au concentrations (from 5mg to 40mg Au/100ml) (**right:** particles size distribution evaluated by Nanotrac wave analyser, **left:** TEM images of the synthesized gold nanoparticles)

The present experiments synthesized gold nanoparticles via the citrate reduction method. Uniform spherical gold nanoparticles around 10nm, 25nm, and 50nm were successfully produced. Results suggested the optimized experimental conditions that at comparatively higher molar ratio of $Na_3C_6H_5O_7$/Au from 1.63 to 2.72, and under the condition that Au concentration is lower than 10mg/100ml, there is the tendency of formation for smaller and uniform spherical gold nanoparticles.

3.2. The $NaBH_4$ reduction method

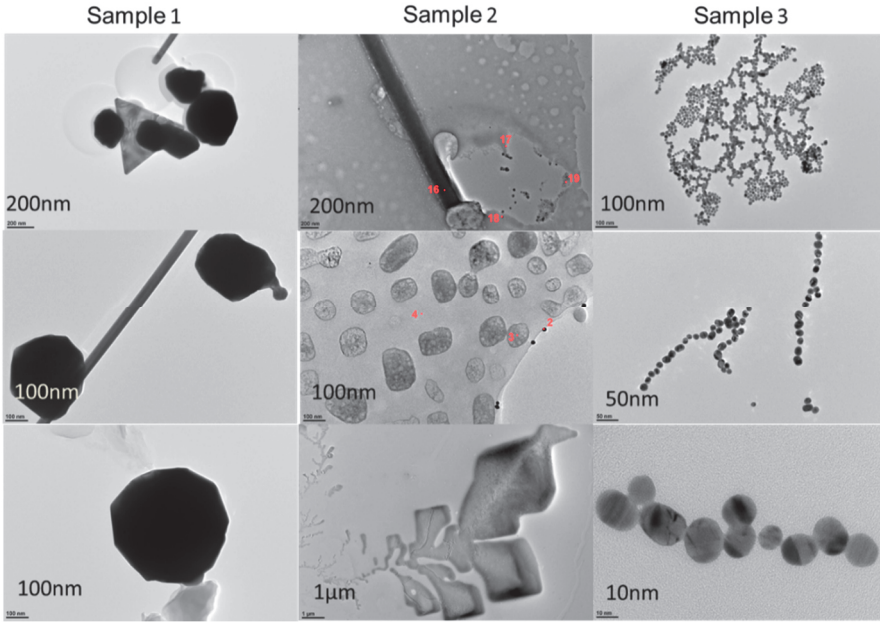


Fig. 4 Different morphologies of gold nanoparticles via $NaBH_4$ reduction method with different reaction parameters (TEM analysis) **Sample 1:** with high reaction rate, **Sample 2:** with modified reaction rate, **Sample 3:** with controlled low reaction rate

In a single-phase reaction system in aqueous solutions, the key point for this synthesis is the rate of reduction. The rate was controlled by the concentration of reductant ($NaBH_4$) and precursors ($HAuCl_4$), the reaction temperature and the addition rate. From sample 1 to sample 3, the concentration of Au and $NaBH_4$ were diluted respectively to 10times and 50times. With the higher concentration of both Au and $NaBH_4$, the reduction rate is very fast and generous irregularly shaped gold nanoparticle, showed by TEM figures, we could find in sample 1 nanorods, triangles, and irregular shapes. In sample 2, the Au $NaBH_4$ concentration was 10times diluted, the $NaBH_4$ concentration was 5times diluted, and the reaction temperatures were optimized from room temperature to 0°C, small gold nanoparticles showed up, still with irregular shaped gold nanoparticles in a big portion. In sample 3, with 10 times diluted Au and 50 times diluted $NaBH_4$, and a reaction temperature at 0°C, gold nanoparticles were synthesized under control with good qualities.

3.3. Post-treatment

The citrate reduction method and the $NaBH_4$ reduction method produce gold nanoparticles with impurities of unreacted sodium ions, salts, excessive citrates and byproducts. A proper post treatment is necessary to access stable and purity gold nanoparticles.

Dialysis was applied to purify the citrate stabilized gold nanoparticles and the experiments last for around one week and samples along time are analyzed by ICP measurements. Results showed an effective purification for the first 48 hours for the citrate reduced gold nanoparticles and higher degree of purity could be achieved through the dialysis method. The decline of Au concentration may course by the exclusion of the unreacted gold precursor.

Table 2 ICP results for gold nanoparticles samples with different particle size purified by dialysis through time (mg/L)

Mean particle size(nm)	0h			24h			48h		
	Au	Na	Cl	Au	Na	Cl	Au	Na	Cl
23.9	117	90	95				94	1	16
37.7	100	53	90.6						
9.6	113	296	10.8						
37.7	118	38.8	77.8	53.3	2.77	3.1	41.1	0.65	0.4

Mean particle size(nm)	96h			144h			168h		
	Au	Na	Cl	Au	Na	Cl	Au	Na	Cl
23.9									
37.7				94	7	0.94			
9.6				81	6	0.04			
37.7	44.8	0.15	0.3				31.4	0.1	0.3

3.4. Stability study

Dialysis process showed their abilities to remove these impurities but the exclusive of the free ligands existed in the solution may cause unexpected affections to the stability of the gold nanoparticles in aqueous solutions. The growth statues during the dialysis process were studied.

Fig. 5 showed the comparison plots analyzed by Nanotrac wave analyzer, indicated consistence results with the observation from color changes. Both of the dialysis and non-dialysis sample suffered particle size distribution changes through time, the particle size distributions were slightly grow up after the 7 days dialysis experiment, particles without dialysis experiment shows a similar tendency. The 48 hours dialysis processes have good affection to gold nanoparticles stability status, especially for $NaBH_4$ reduced gold nanoparticles.

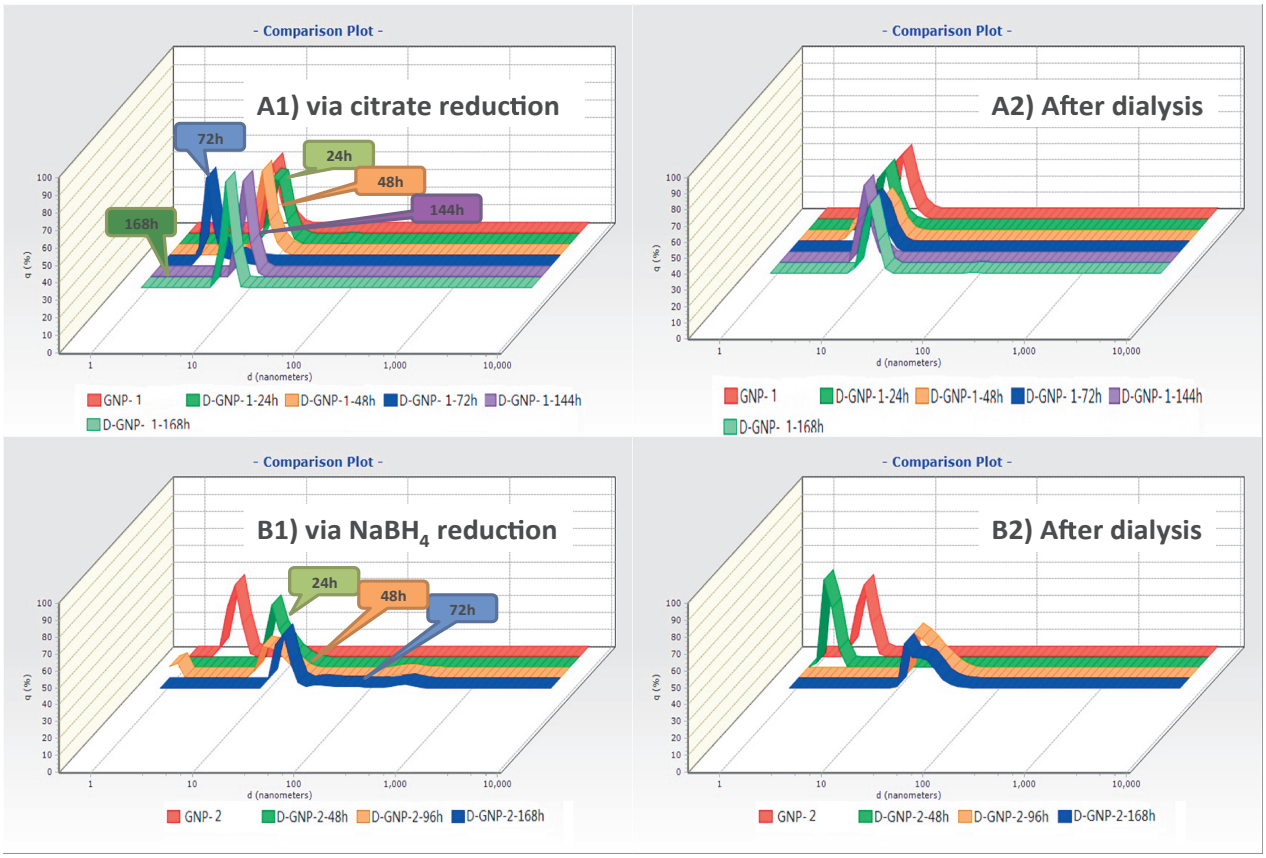


Fig. 5 Gold nanoparticle changes after dialysis experiment through time evaluated by Nanotrac wave analyzer (**A:** gold nanoparticle synthesized via citrate reduction method, **B:** gold nanoparticles synthesized via $NaBH_4$ reduction method)

4. CONCLUSIONS

The present article is of great advantage for the productions of gold nanoparticles in the near future. The protocol from the citrate reduction method and the $NaBH_4$ reduction method is very straightforward, and Gold nanoparticles with spherical morphology around 10nm were successfully fabricated via the citrated reduction method and the $NaBH_4$ reduction method. With the progress made from the synthesis process, we got good results for gold nanoparticles both in quality and quantity.

For the citrate reduction process, the influence of citrate and Au concentration and reaction temperature are studied as key parameters. Results reveal the interrelationship between each parameter. Stable and uniform gold nanoparticle could be synthesized when the Au initial concentration is lower than 40mg/100ml. The citrate concentration as the most important factor, is not only an important function of the final particle size distribution, but could also act as an agent to modify the affection of the reaction temperature.

Synthetic procedure with reductant $NaBH_4$ in single aqueous solutions has been studied. Since this procedure is different with the Brust process where the reduction rate is controlled by the phase transfer process at the interface, the control for the reduction rate is very important in the process. Optimized experimental parameters have been set up, and the process has successfully been scale up.

Post treatment for citrate stabilized gold nanoparticles is studied by dialysis method. As one of the traditional separation method, dialysis showed their reliable results to get purity gold nanoparticles. Our study showed 48 hours dialysis could decrease the impurities by large portion, and at the same time could improve the quality of the citrate stabilized gold nanoparticles. Prolong the detention time could assume high degree of purification, but will sacrifice the quality of gold nanoparticles.

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REFERENCES

[1] A. De, R. Bose, A. Kumar, and S. Mozumdar, "A Brief Overview of Nanotechnology," *Targeted Delivery of Pesticides Using Biodegradable Polymeric Nanoparticles*, SpringerBriefs in Molecular Science, pp. 35-36: Springer India, 2014.

[2] M.-C. Daniel, and D. Astruc, “Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology,” *Chemical reviews,* vol. 104, no. 1, pp. 293-346, 2004/01//, 2004.

[3] J. H. T. Luong, K. B. Male, and J. D. Glennon, “Biosensor technology: Technology push versus market pull,” *Biotechnology Advances,* vol. 26, no. 5, pp. 492-500, 9//, 2008.

[4] F. Schulz, T. Homolka, N. G. Bastus, V. Puntes, H. Weller, and T. Vossmeyer, “Little adjustments significantly improve the turkevich synthesis of gold nanoparticles,” *Langmuir,* vol. 30, no. 35, pp. 10779-84, Sep 9, 2014.

[5] J. W. Park, and J. S. Shumaker-Parry, “Structural study of citrate layers on gold nanoparticles: role of intermolecular interactions in stabilizing nanoparticles,” *J Am Chem Soc,* vol. 136, no. 5, pp. 1907-21, Feb 5, 2014.

[6] M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, and C. Kiely, “Synthesis and reactions of functionalised gold nanoparticles,” *Journal of the Chemical Society, Chemical Communications*, no. 16, pp. 1655-1656, 1995.

[7] S. M. Ansar, F. S. Ameer, W. Hu, S. Zou, C. U. Pittman, Jr., and D. Zhang, “Removal of molecular adsorbates on gold nanoparticles using sodium borohydride in water,” *Nano Lett,* vol. 13, no. 3, pp. 1226-9, Mar 13, 2013.