



The effects of microgravity on nanoparticle size distributions generated by the ultrasonic reduction of an aqueous gold-chloride solution

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Abstract

A solution of gold chloride was reduced using ultrasound irradiation to prepare metallic gold nanoparticles under conditions of microgravity and normal gravity at sea level. Particle size distributions were measured using TEM analysis. A mean particle diameter of 10 nm was obtained in microgravity while a mean diameter of 80 nm was obtained in the laboratory. Absorbance measurements on the reacted solution found an enhanced reduction rate in the reduction of gold chloride in microgravity compared to that in the laboratory.

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1. Introduction

The formation of nanosized metallic particles has attracted much attention over the last decade because of a number of discoveries regarding their unique physical and chemical properties [1,2]. The small sizes of these particles makes them ideal catalysts for chemical reactions and recent studies have shown that these nanosized particles can be used to form quantum dots [2]. Therefore it has become important to understand the preparation of these particles and develop techniques to alter their concentration and geometric properties.

Considerable research has gone into the formation of nanosized noble metals by ultrasonic irradiation of aqueous solutions [3–5]. When a solution is exposed to ultrasound of sufficient intensity a cavitation field is formed made up of a large distribution of vapor and gas-filled bubbles, which pulsate due to the driving

acoustic field. When the pressure inside the bubble falls below the vapor pressure of the liquid the bubble fills with vapor and grows. The bubble then collapses inward when the pressure turns positive, resulting in extreme temperatures and pressures in the interior of the bubble. The resulting local hot spots lead to the dissociation of molecular species within the interior of the collapsing bubble. In the case of water vapor this dissociation results in the production of H and OH radicals [3]. The radicals produced in the interior of the bubble can then diffuse into the bulk solution and reduce metal ions yielding nanosized metallic particles. Although additional radicals can be produced in the surrounding solution due to the presence of a stabilizer such as a water-soluble polymer, it is realized that these reactions are dominated by the initial formation of radicals in the interior of the collapsing bubble [4]. Even though the sonochemical reduction mechanisms for these noble metal particles are relatively well known [3,4,10], making particular sizes and geometrical properties of the nanoparticles are more of an art form than science.

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Recent work has been carried out in the effects of microgravity on sonoluminescing bubbles [6,7], and it is hypothesized that bubbles in an applied acoustic field can be made to collapse more violently when buoyancy is removed, as is the case during a microgravity environment. That is, instabilities may limit the energy concentration as the bubble collapses [8,9], and buoyancy-driven instabilities may be the dominant mechanism [7]. In the case of radical production in the interior of the bubble, a natural question is then “does buoyancy affect the collapse of bubbles in a cavitation field, and the associated formation of radicals, and if so, how does this change alter the properties of the nanoparticles?”

In this article we examine the effects that a microgravity environment has on the reduction of an aqueous solution and the geometric properties of the formed nanoparticles. The microgravity results are then compared to earth-based laboratory results.

2. Experimental study of sonochemistry in a microgravity environment

Investigation into the effects of a microgravity environment on the reduction of a gold-chloride solution and the resulting gold nanoparticles was carried out on NASA's parabolic research aircraft. Parabolic trajectories flown by the aircraft produce brief periods of microgravity (<0.04 g) lasting for approximately 20–25 s, followed by a hyper-gravity region (≈ 1.8 g). The initial transition into the microgravity phase lasted several seconds. A relatively stable microgravity period was then followed by longer-duration hyper-gravity phases. During each of two flights, the aircraft underwent approximately 30 such parabolic trajectories.

The primary objective of this experiment was to determine if the reduction in gravity played a significant role in the reduction of a gold-chloride solution into gold nanoparticles, and what a change in this reduction process would have on the geometric properties of the nanosized gold metal particles.

A 90 ml sample solution of 1 mM gold chloride (HAuCl_4) and 0.13 mM polyethylene glycol (PEG) was placed in a cylindrical stainless steel vessel (diameter: 3.6 cm; depth: 10.2 cm). Overflowing the solution as the ultrasonic horn tip was inserted into the vessel purged any excess air. The vessel was sealed using an o-ring and two pressure locking bolts. Ultrasonic irradiation was performed with a model VCX400 Vibra Cell along with a model CV26 ultrasonic horn, both purchased from Sonics and Materials Inc. The horn operated at 20 kHz and 11.8 W/cm^2 . The PEG was used as a steric stabilizer for the colloidal particles formed during irradiation.

During the flight a program written in LabView monitored acceleration data and controlled the activation of the horn. When the accelerometer read between

0.07 and -0.07 g the program initiated a 6 s delay followed by a 6 s irradiation period. The delay allowed for pilot correction during the onset of microgravity and insured that the horn operated during a region of relatively stable microgravity. The program recorded all acceleration data, temperature data, and horn operation intervals.

Preparation of gold nanoparticles using this same method was performed at sea level under 1 g conditions in order to compare the results with those of the microgravity experiments. A LabView program used the flight-obtained accelerometer data to duplicate the flight irradiation intervals. Analysis of the flight experiment could not be performed on sight due to budget constraints. The samples had to be shipped back to the University of Washington from Ellington Field in Houston, Texas. The results were therefore not recorded until 14 days after the flight days. Analysis of the ground experiment samples were thus also carried out 14 days after their formation. This was done to insure that all controllable parameters were duplicated as exactly as possible.

2.1. Absorption measurements

Absorbance spectra were recorded on a Shimadzu UV-1601 spectrometer operating from 290 to 800 nm. The absorbance measurements were recorded for all solutions prepared above.

2.2. Electron microscopy measurements

TEM photographs were taken with a Philips 400 TEM. Samples were prepared by placing a drop of the suspension on a carbon coated copper TEM grid using a micropipette. The suspension drop was air dried for 3 h then vacuum stored at 10^{-2} Torr for >2 h. Images were taken at 100 keV at magnifications of 60–480k.

3. Results

3.1. Experimental operation

The flight profile of the parabolic research aircraft, shown in Fig. 1a, generates variable accelerations. A typical profile of the accelerometer data is shown in Fig. 1b. The aircraft begins the parabola with a full-throttle elevation gain, resulting in accelerations reaching approximately 1.8 g. The aircraft then transitions into a microgravity phase as it begins a freefall. After approximately 20–25 s, it pulls out of the freefall, again generating about 1.8 g. The ultrasonic horn is operated for 6 s during a relatively stable portion of the microgravity phase, as shown by the dashed lines in Fig. 1b. Because of the relatively short operational period, the

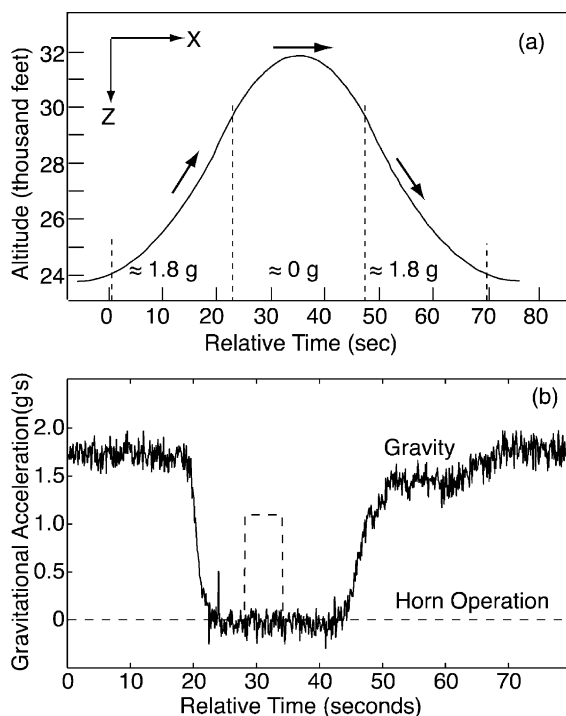


Fig. 1. (a) An illustration of the parabolic trajectory flown by the parabolic research aircraft. Approximately 20–25 s of microgravity are achieved during each parabola. (b) An example of the gravitational acceleration and ultrasonic horn operation for flight 1. The solid line is the acceleration obtained from the accelerometer. The dashed line indicates the on and off-times of the ultrasonic horn. The horn was operational only during a portion of the microgravity region.

temperature of the liquid does not vary much. Table 1 shows typical temperatures as measured with a thermocouple probe.

3.2. Absorption measurements

Absorption traces from the two flight experiments and the corresponding ground experiments, taken 14 days after the experiment for each case, are shown in Fig. 2. Each trace has two absorption bands, one centered between 280 and 300 nm, and one centered between 540 and 560 nm. The position of the first maxima is the characteristic absorbance peak for AuCl_4 and is attributed to the gold chloride remaining in solution after irradiation. The second peak is due to the existence of gold nanoparticles in solution. A decrease in this second peak is due to particles falling out of solution, as was evident by visual inspection of aggregate clusters on

Table 1
The starting and final temperatures for flight and ground experiments

	Ground 1	Ground 2	Flight 1	Flight 2
Start temperature ($^{\circ}\text{C}$)	22.9	22.9	20.8	20.8
Final temperature ($^{\circ}\text{C}$)	27.3	27.3	24.4	22.5

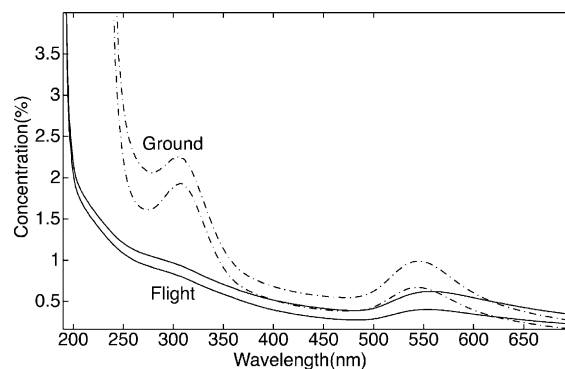


Fig. 2. Absorbance spectra from two separate ground (---) and flight (—) experiments. The spectra contains two peaks, one centered near 320 nm, which shows the remaining gold chloride in solution. The second peak is centered near 550 nm as is indicative of the existence of gold nanoparticles.

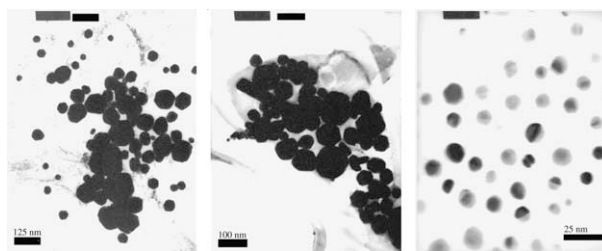


Fig. 3. Left to right: TEM photos taken for ground (125 nm scale) and flight (100 and 25 nm scale). The smallest particles were unique to the microgravity environment.

the bottom of the vessel. However, the peak centered around 550 nm is not an accurate measure of the concentration of gold nanoparticles, because variations in their size and shape can produce alterations in the absorbance spectrum [5].

3.3. Electron microscopy (TEM)

Example transmission electron micrograph photos are shown for both the flight and corresponding ground experiments in Fig. 3. A magnification of 60k was used for the ground experiment. Smaller particles were not found at higher magnifications. Scans from 60 to 480k were performed on both samples. Magnifications of 80 and 480k yielded particle images for the flight samples. A relatively broad size distribution is clear in each image. The size distribution for these images is shown in Fig. 4.

4. Discussion

The results of Figs. 2 and 3 indicate that a microgravity environment may in fact have a significant effect

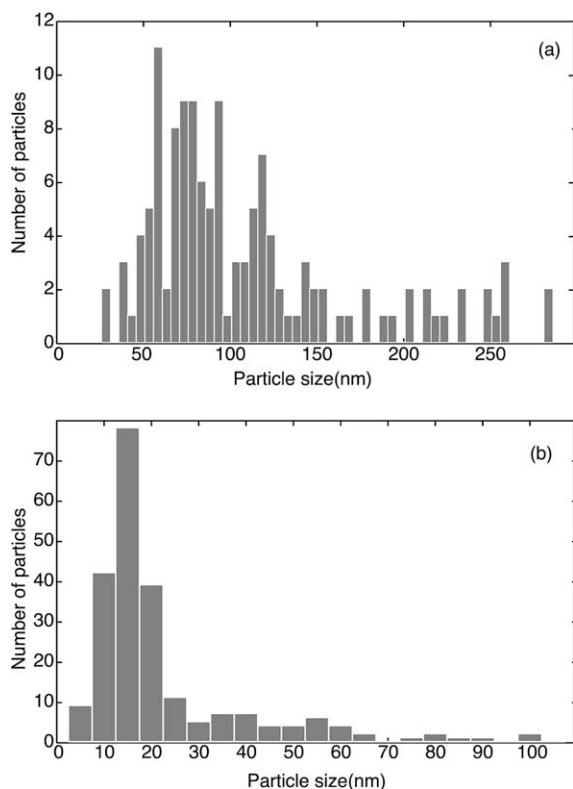


Fig. 4. Size distributions of gold nanoparticles for a typical ground experiment (a), and flight experiment (b). Clearly, the microgravity-generated gold nanoparticles have a smaller size distribution.

on both the reduction of gold chloride, and on the size of nanoparticles formed during this reduction. The observed absorption maximum at 300 nm shown in Fig. 2 indicates a dramatic decrease in the remaining gold chloride for the two flight experiments. This decrease in the absorption band centered around 290 nm indicates that when irradiation is applied to an aqueous solution while in microgravity an increase in the rate of reduction may be achieved. The TEM photographs of the nanoparticles formed during these reactions show that smaller particles may be formed while in the microgravity environment. While the exact mechanisms that led to these changes are expected to be highly complex [10] and are beyond the scope of the experiments we performed, it is evident that a change during microgravity did occur.

It is possible that the reduction of buoyancy-driven instabilities resulted in a more violent collapse of the cavitation bubbles, resulting in an increased production of radicals in the interior of the bubble. The increase in the number of radicals would result in an enhanced rate of reduction of the gold chloride. It is also possible that this increase in radical initiated reduction of the solution may result in the observed alteration of the particle sizes found during the flight. It is not possible to determine if the change in reduction rate caused the for-

mation of the observed smaller nanoparticles, without changing a controlled experimental variable. However, it is widely accepted [5,10] that the existence of small spherical nanoparticles causes an increase in reduction rate. Small spherical nanospheres in an aqueous solution can act as seed nuclei for crystal growth [5]. The presence of these small nanospheres such as those in Fig. 3c would result in large anisometric particle growth from the remaining gold-chloride solution, causing a decrease in the absorption band around 300 nm.

Other possible explanations for the observed changes in gold chloride reduction and nanoparticle size may come from experimental variations due to the complex nature of experiments in a variable-gravity laboratory. These issues are as follows:

(1) It was observed after each flight that a small amount of solution had seeped out of the chamber. It was later confirmed that the pressure release valve (installed as a safety requirement for NASA) had a hairline crack possibly preventing the chamber from being perfectly sealed. The cabin pressure on the reduced gravity aircraft is set at 565 mmHg, which results in a 25.6% decrease in ambient pressure relative to the ambient pressure of the experiments carried out at sea level where the pressure is at 760 mmHg. This change in the ambient pressure might affect the growth of the cavitation bubbles based on gas diffusion models. The question of whether this 25.6% decrease in ambient pressure would be enough to generate the changes we observed is yet to be answered.

(2) It is also possible that the cavitation field generated by the ultrasonic horn was different in microgravity. Because buoyancy is almost absent, bubbles formed in microgravity may not flow from the horn tip as they might in a buoyant gravitational field. The changes in the fluid loading on the horn tip may account for the differences observed.

(3) Although there were temperature changes in our system, the changes were small, and probably did not affect the results.

To summarize, it is clear that the microgravity environment had a distinct effect on the reduction of gold chloride and the size of nanoparticles formed from this reaction. Whether the change in ambient pressure, changes in fluid loading, or the variations in temperature were of any significant influence is still uncertain. Further studies are needed to quantify these possible effects. If the influence of gravitational acceleration can be verified to play a significant role on the concentration and geometric properties of nanoparticles formed by ultrasonic irradiation, it may become possible to better understand the effects of ultrasound on the sizes and shapes of the nanoparticles. This would be useful in understanding the physical properties of these particles, and would lead to more exciting applications of

nanoparticles formed by ultrasonic irradiation techniques.

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References

- [1] B.V. Volovik, *Semiconductors* 33 (1999) 901.
- [2] M.V. Maximov, *Microelectron. Eng.* 51/52 (2000) 61.
- [3] F. Grieser, *Stud. Surf. Sci. Catal.* 103 (1996) 57.
- [4] K. Okitsu, Y. Mizukoshi, H. Bandow, Y. Maeda, T. Yamamoto, Y. Nagata, *Ultrason. Sonochem.* 3 (1996) 249.
- [5] J. Wiesner, A. Wokaun, *Chem. Phys. Lett.* 157 (1989) 569.
- [6] T.J. Matula, *Ultrasonics* 38 (2000) 559.
- [7] T.J. Matula, V.J. Bezzerides, P.R. Hilmo, L.N. Couret, T.W. Olson, L.A. Crum, *Acoust. Soc. Am.* 1 (2000) 13.
- [8] R.M. Davies, G.I. Taylor, *Proc. Roy. Soc. Lond. A* 200 (1950) 375.
- [9] M.S. Longuet-Higgins, H. Oguz, *J. Fluid. Mech.* 290 (1995) 183.
- [10] R.A. Caruso, M. Ashokkumar, F. Grieser, *Langmuir* 18 (2002) 7831.