

# Nanoparticles: Synthesis and Film Deposition Using a Simple and Fast Centrifuge Sedimentation Method

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## ABSTRACT

Methods to deposit nanoparticles (NPs) on a variety of platforms are a major step towards nano-technology development. In this study, Gold (Au) nanoparticles (NPs) were synthesized by a water-in-oil microemulsion method using a reducing agent and a capping reagent. Semiconductor quantum dots (QDs), such as lead sulfide (PbS), were fabricated via an organic chemical synthesis method. An alternative, facile and swift NP deposition method is described which utilizes only a standard centrifuge instrument and common solvents. This centrifuge deposition method (CDM) is a very simple and efficient process that can be applied to a wide variety of substrates and different NPs. It allows good coverage and thickness control of the NP films and layer by layer deposition of different NPs in a very simple manner.

**Keywords:** synthesis, film, centrifugation, deposition, fast

## 1 INTRODUCTION

Current procedures for depositing NPs on solid surfaces include chemical vapor deposition [1], physical vapor deposition [2], sputtering [3], lithography [4], spin coating [5], pulsed laser deposition [6] and supercritical fluid CO<sub>2</sub> deposition [7,8]. Most NP deposition techniques require specific equipment and a high level of technical expertise. Centrifugal deposition method has been used and reported previously for making a thin film. However, little has been explored in using centrifuge deposition for nanoparticle film formation. In this study, a facile and rapid NP deposition method is described which utilizes only a standard centrifuge instrument and common solvents for fabrication of NP films. A wide variety of substrates including glass, silicon wafer, aluminum foil, copper sheet, polymer film, paper, etc. and different nanoparticles were applied. Gold and PbS NPs were arbitrarily selected for this study. This method also shows the deposition can take place on flexible or rough surfaces, not limited to flat surfaces, such as flexible black plastic, aluminum foil, copper sheet, etc. This method offers a fast and simple procedure compared to other currently known nanoparticle deposition techniques for studying properties of nanoparticle films.

## 2 EXPERIMENTAL

Gold NPs were prepared by reduction of gold ions suspended in sodium *bis*(2-ethylhexyl)sulfosuccinate (AOT) water-in-hexane microemulsions with another AOT microemulsion containing a reducing agent NaCNBH<sub>3</sub>. The size of the Au NPs can be controlled by the *W* value (water/surfactant molar ratio) of the microemulsions and by the NP protecting agent dodecanethiol [9].

Oleic acid-capped PbS NPs were prepared by a reaction of PbO with *bis*(trimethylsilyl)sulfide (TMS), oleic acid (OA) and octadecene (ODE). The molar ratio of OA:PbO:TMS used was 4:2:1. The sizes of PbS NPs can be controlled by the injection and reaction temperatures and the molar ratio of OA/PbO.

Colloidal Au or PbS NPs synthesized can be deposited uniformly on flat substrate surfaces employing a standard centrifuge and common solvents. Different substrates were chosen for the deposition of Au and PbS NPs, which included rigid, flexible, conductive, and insulating materials such as a plastic sheet [polyethylene terephthalate (PET)], aluminum foil, copper sheet, copper grid, flexible black plastic [6 μm, high-density polyethylene (HDPE)], glass slide, paper and silicon. Figure 1 shows some representative substrates used in this study for metal NP (Au and Pt) and semiconductor PbS quantum dot coatings. Transmission electron microscope (TEM) images were obtained from TEM Cu grids which were loaded with these substrates under the same experimental conditions and deposited with Au, or PbS NPs. Scanning electron microscope (SEM)

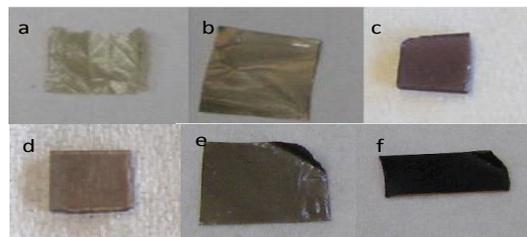


Figure 1: Nanoparticles deposited by the CDM on different substrates. a) PbS NPs on HDPE, b) PbS NPs on aluminum foil, c) Au NPs on glass, d) Pt NPs on glass, e) PbS NPs on Au NPs on aluminum foil. f) PbS NPs (4.7 nm) on Au NPs (14.4 nm) on Au NPs on copper substrate.

images of the Au and PbS NPs deposited on these substrates were also obtained. However, in this study, our emphasis is focused on the exploration of CDM method using Au and PbS NPs.

A general procedure for depositing different colloidal nanoparticle samples using the centrifugation approach is described below. About 625  $\mu\text{L}$  of Au nanoparticle solution ( $\sim 0.005\text{ M}$ ) in hexane were mixed with 5 mL of absolute ethanol. A desired substrate was placed in the bottom of a vial. The vial was then placed in a standard centrifuge with swinging basket and spun for 8 min at 3,400 rpm. Before CDM, the sample was sonicated for a half min making sure the NPs were dispersed well in hexane and methanol (or ethanol) mixed solutions. After centrifugation, the colorless supernatant was pipetted out and the substrate with the deposited Au NPs was then removed and allowed to air dry for future measurements.

A procedure was also developed for depositing PbS NPs. The deposition method used is similar to the Au NP deposition. 20  $\mu\text{L}$  of PbS (depending on the concentration synthesized) plus 50  $\mu\text{L}$  of toluene were first mixed to prevent premature precipitation, which could lead to uneven coverage. One mL of methanol was then added to make the particles less soluble in the solution. The vial was then placed in a centrifuge tube and spun, depositing the particles on a substrate placed on the bottom of the vial. Using a standard laboratory centrifuge at 3,400 rpm, which produces approximately 1,950 G, the deposition of 4.8 nm PbS particles was complete. However, we found that NP solutions with NP size less than 2.7 nm were still somewhat colorful, indicating only a partial deposition occurred. An ultra-centrifuge at 10,000 rpm producing over 15,000 G was utilized for the deposition of the nanoparticles less than 2.7 nm.

The TEM samples were prepared by CDM. A Phillips CM 200 LaB<sub>6</sub> (Lanthanum Hexaboride Cathode) TEM operating at 200 kV was used. The average size of the PbS NPs was obtained from the TEM images by measuring at least 300 particles using the ImageJ software.

SEM images were collected with a Sirion instrument manufactured by FEI, Inc. The following parameters were used for the SEM field emission gun (FEG): an accelerating voltage of 5 kV, a spot size of 3.0, and a working distance of  $\sim 4.5\text{ mm}$ .

To define the boundary of a NP layer when measuring the NP layer cross section, NOVA SEM (FEI NOVA NanoLab 600 FIB) instrument was employed for injecting SEM glue (Kleindiek NanoTechnik, SEM GLU) onto a corner of the Si substrate, a small amount of which was then transferred onto the top layer of the nanoparticles. In this process the SEM glue penetrated into the top layer of QDs to make the QD layer stiff. A FEI Sirion SEM instrument in conjunction with a back scattering electron (BSE) detector was used, which offers a better definition and contrast between the Au and PbS nanoparticle layers. BSE images are very helpful for obtaining high-resolution compositional maps of a sample and for quickly distinguishing different phases

during the measurement of the cross section of different layers of the films.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Synthesis of Au NPs Using Microemulsions

Gold particles were prepared by reduction of gold cations suspended in AOT water-in-hexane microemulsions. Separate metal ion and freshly prepared reducing agent solutions were prepared by dissolving 0.0178 g of AOT in 2 mL of hexane and adding an aqueous solution of 7.2  $\mu\text{L}$  (water/surfactant molar ratio,  $W = 10$ ) of either the 0.4 M Au<sup>3+</sup> gold ion or the 1.2 M NaCNBH<sub>3</sub> reducing agent. These micellar solutions were stirred for 1 h before reduction to equilibrate the reagents to the reaction temperature. The microemulsion containing the reducing agent was added dropwise over a time span of 60 sec to the gold ion-containing microemulsion. With vigorous stirring, microemulsions were formed which appeared transparent to the naked eye. The size of the microemulsion is related to the molar ratio of the  $W$  value by the following equation:

$$R_{\text{radius (nm)}} = 0.175W + 1.5$$

where  $R$  is the radius of the water core. Chemical reduction of the metal ions is accomplished by addition of the reducing agent NaCNBH<sub>3</sub> to the solution. Bubbling hydrogen gas through the microemulsion solution is another way of reducing the metals ions to their elemental state. Dodecanethiol (70  $\mu\text{L}$ ) was added to the reaction immediately after all of the reducing agent had been added to the solution. This solution was then allowed to stir at room temperature for another hour. The gold particles were then precipitated by adding a mixture of 6 mL of ethanol and 4 mL of methanol, followed by centrifugation. The supernatant was discarded, and the remaining particles were washed two more times with 5 mL of ethanol to remove AOT, spectator ions, and excess dodecanethiol. Multiple sets of the particle samples were combined, re-suspended in 1 mL of toluene or

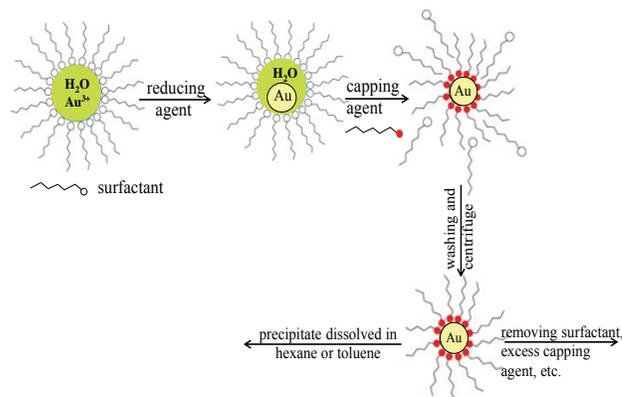


Figure 2: Synthesis of metal nanoparticles using the microemulsion method.

hexane, and the final concentration was approximately 0.005 M. All procedures were conducted on the benchtop without the need for inert environments (Figure 2).

### 3.2 Synthesis of PbS QDs

The microemulsion technique, however, does not work for synthesis of PbS NPs according to our experiments. The reason is likely due to the fact that the aqueous chemistry of lead ions is complicated and various lead species can exist in water depending on pH value and redox environments. Therefore, it is difficult to control the dissolved lead ions in the water core of the microemulsion in the pure  $Pb^{2+}$  state. We chose to synthesize PbS NPs in organic solvents with oleic acid as a capping agent.

Oleic acid-capped PbS NPs were prepared, in principle, in a similar manner to Hines et al. [10], but with some modifications. 0.25 mL ( $0.8 \times 10^{-3}$  mol) oleic acid, 0.09 g PbO ( $0.4 \times 10^{-3}$  mol), and 42  $\mu$ L of TMS ( $0.2 \times 10^{-3}$  mol), were used, at a molar ratio of 4:2:1. PbO (0.09 g), ODE (3.9 mL) and OA (0.25 mL) were added in a 3 neck-reaction flask and vigorously stirred, under a flow of continuous argon (Ar) gas at 150 °C for 1 h. After 1 h, TMS (42  $\mu$ L) dissolved in 2 mL of ODE were quickly injected at 150 °C into the reaction flask, while the magnetic stirrer was vigorously stirring and Ar gas was continuously passing through. The solution color changed from colorless to dark brown immediately. The heating source was removed and the temperature reduced to 100-120 °C. The temperature of the system was kept at this temperature range and the stirring continued under Ar gas for another hour.

The sample was washed in absolute 200 proof ethanol 3 to 4 times and methanol one time using a 8 mL glass vial until the dark brown lower organic phase disappeared, and black PbS QDs were completely precipitated. The NPs were dried with a stream of  $N_2$  and then dissolved in toluene.

### 3.3 Deposition of NPs Using CDM

Gold and PbS NPs can be homogeneously deposited on a TEM carbon coated copper grid using the CDM method. Figure 3 shows a TEM image of Au NPs (3.1 nm) deposited by CDM on copper grids with monolayer arrangement

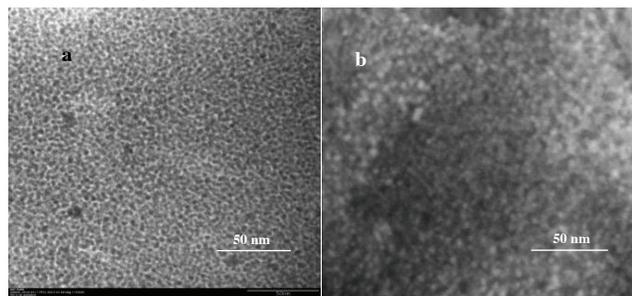


Figure 3: (a) TEM images of Au NPs ( $3.1 \pm 0.34$  nm) deposited on carbon coated Cu grids by CDM. (b) SEM image of Au NPs ( $3.1 \pm 0.34$  nm) on copper sheet.

(Figure 3a) and a SEM image of Au NPs deposited on copper sheet in multilayer arrangement (Figure 3b). The thickness of the film can be varied by changing the concentration, or the volume of the NP solution. The surface morphology of these films is comparable to the PbS QD arrays achieved by a supercritical  $CO_2$  fluid deposition process [7,8] including those reported on a GaAs substrate [11]. In general, the images of the Au and PbS NP films deposited by the CDM procedure reveal fairly homogenous coverage on different substrates.

To demonstrate the fabrication of double-layer films on a solid surface, a single layer of Au NPs was deposited on a piece of silicon, and the remaining liquid was then pipetted out. The sample was left to dry overnight. After that, a second solution containing PbS NPs was added and the CDM procedure was repeated to make the second layer. Figure 4 shows cross sections of SEM images of a single Au NP layer ( $\sim 400$  nm) deposited by CDM (Figure 4a), and a double-layer film (Figure 4b) made with a PbS NP layer (4.7 nm,  $\sim$  thickness of 500 nm) deposited on the top of the Au NP layer (2.2 nm,  $\sim$  thickness of 430 nm) applying the CDM procedure. The back scattering electron detector shows the SEM image with distinct contrast between the two layers (Figure 4).

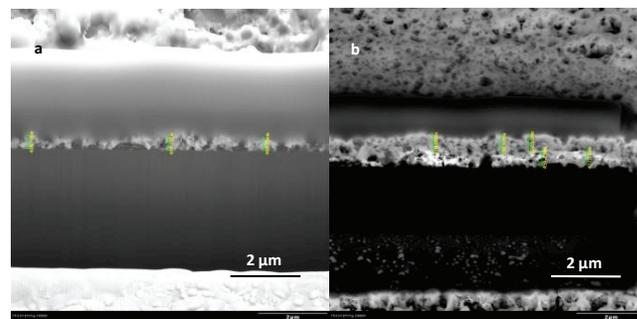


Figure 4: SEM images of (a) a cross section of a single Au layer film, the thickness is  $\sim 400$  nm, (b) a cross section of a double layer film, the thickness of Au layer (bottom) is about 430 nm, and PbS layer (top) is about 500 nm. The green lines shown on the cross section in SEM images are measuring bars.

Control of film coverage at low population of NPs was demonstrated by TEM images. Figure 5 shows when the volume of Au NPs added increases, the coverage or the thickness of the Au NPs in the CDM process can be increased as well. As shown in Figure 5a when 10  $\mu$ L of Au NPs were used, the films (on TEM grids) showed randomly scattered islands, indicating that NPs used were not crowded enough. When 20  $\mu$ L (Figure 5b) and 80  $\mu$ L (Figure 5c) Au NPs were added separately in CDM, relatively dense (Figure 5b), and an monolayer (Figure 5c) distributions could be observed. When more Au NPs, for example, 200  $\mu$ L (Figure 5d), were added in CDM process, thick films can be formed. However, the multilayer creates a hindrance for clear

observation of NPs from TEM. For Figure 5d, when a 200  $\mu\text{L}$  NP solution was added, an area at the edge of uniform coverage was selected where the voids allow the film thickness to be imaged. Nevertheless, the process of the film formation by CDM with increasing amount of the Au NPs is clearly illustrated in Figure 5.

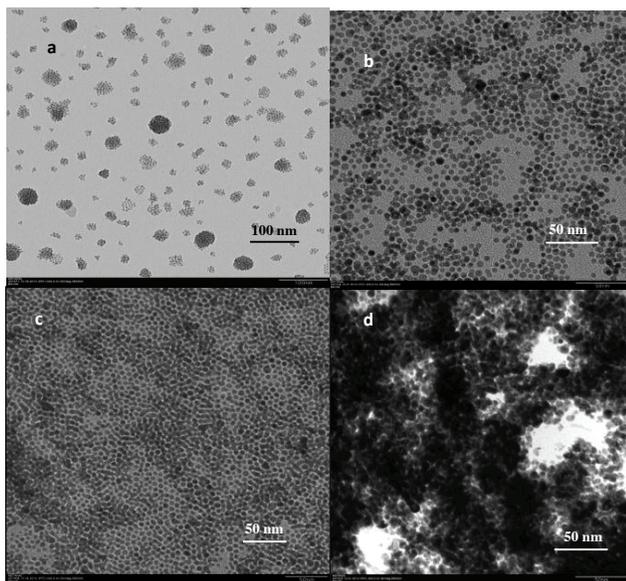


Figure 5: TEM images of (a) 10  $\mu\text{L}$ , (b) 20  $\mu\text{L}$ , (c) 80  $\mu\text{L}$  and (d) 200  $\mu\text{L}$  Au NPs added in CDM processes.

The cross sections of the Au film were measured by SEM as shown in Figure 6. Au NP volume ratios used for making these films are 1:10:20 (20  $\mu\text{L}$  : 200  $\mu\text{L}$  : 400  $\mu\text{L}$ ). The average cross section thickness of the Au films measured from Sirion SEM instrument in Figure 6a, b, and c were 209 nm, 467 nm, and 952 nm, corresponding to the Au NP solution ratios of 20  $\mu\text{L}$  : 200  $\mu\text{L}$  : 400  $\mu\text{L}$ , respectively. Once a film, at least a monolayer, was formed, the thickness could be controlled with the addition of the known volume of NPs, in which the film thickness is proportional to the NP volume added. Based upon the thickness data, the thickness ratio for films b and c is quite proportional to the relative amounts of the Au NP solution added, i.e., when the volume of NP solution added in Figure 6b and 6c increases by a factor of 2 (from 200 to 400  $\mu\text{L}$ ), the film thickness doubles from 467 nm to 952 nm. However, from 20  $\mu\text{L}$  to 200  $\mu\text{L}$ , the film thickness acquired is not proportional to the Au NP solution added. This is because the population of the NPs was not high enough to cover the substrate surface (Figure 5a and 5b), and only island-like structures were formed and the cross section of the NP film from SEM image (Figure 6a) was not continuous. Only when the population of the Au NPs is high enough to form at least a monolayer film (Figure 5c), then the thickness of the film is proportional to the volume of NP solution added.

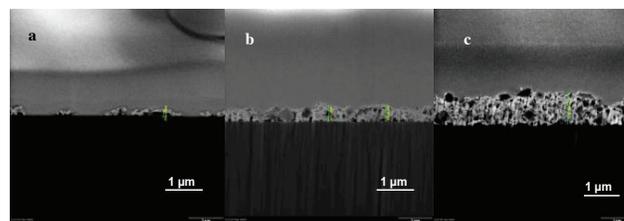


Figure 6: SEM of Au layer cross section, Au NP volume ratios added are 1: 10: 20. SEM magnifications are all 15,000X. Cross sections in Figure 6a, b and c are around 209 nm, 467 nm, and 952 nm, respectively.

All the NPs adhered firmly to the substrates, albeit with different strengths. For example, the Au NP films did not detach from glass substrate when scotch tape was applied. The PbS NPs could be removed from glass directly using scotch tape. However, when a layer of Au NPs was first applied on the glass, the PbS NP layer on top was not readily removed. The adhesion strength of the NP film also varied with the substrates used. The PbS NPs did not come off with scotch tape when deposited on a PET sheet.

This method is suitable for depositing different NPs on a variety of substrates. Thickness of the films can be controlled by the amount of the colloidal nanoparticle solution added. This method offers a fast and simple procedure compared to other currently known nanoparticle deposition techniques for studying properties of nanoparticle films.

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