

THE PENNSYLVANIA STATE UNIVERSITY
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DEPARTMENT OF CHEMICAL ENGINEERING

THE DESIGN AND ASSEMBLY OF DUAL-FUNCTIONALIZED PHOTOACTIVE
COLLOIDS

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Abstract

Dual-functionalized photoactive colloids have a variety of potential applications including photocatalysis, colloidal robotics, and the building of more complex devices. The purpose of this paper is to describe a simple and comprehensive method for fabricating functional colloidal assemblies using a photoresponsive material by manipulating interparticle forces, applying surface modifications, and developing assembly techniques. This is demonstrated using a gold-silicon-silver triplet structure of approximately 5-10 μm .

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Introduction

Part I: Fundamentals of colloidal science

Colloids are small solid particles dispersed in a medium, usually a fluid. They typically range from nanometers to micrometers. Because of this small size, thermal energy induces Brownian motion of the particles, which is a seemingly random motion of these particles in a fluid. Brownian motion plays important roles in the properties of colloidal suspensions. In order to achieve a low-energy ordered structure, interparticle interaction energies of polymers must be around the thermal energy ($k_B T$) in response to Brownian motion. However, interparticle interaction is often far greater than this, in which case the particles form local clusters and networks.¹

This interparticle interaction between two particles is governed by the van der Waals force. If there is no counteracting force, the particles will aggregate and the colloidal system will be destabilized. Colloidal stability is achieved due to repulsive forces balancing the attraction forces. Electrostatic stabilization involves repulsive Coulomb forces acting between negatively charged colloidal particles, and thus balancing the van der Waals forces.

Van der Hoff developed the original process for synthesizing polymer colloids, in which a monomer and catalyst are added to a previously prepared latex. In his process, a mathematical relationship between particle volume increase and ultimate particle size was also determined.² Since then, these devices have been increasingly important in various areas of technology and

research. An excellent example of this is the use of polymer colloids as coatings, which have a wide variety of applications ranging from protective finishes on large industrial structures to aesthetic appeal.³

Colloidal gold is a suspension of sub-micrometer sized particles of gold in a fluid. For particles less than 100 nm, the liquid is usually deep red in color. Michael Faraday, an English chemist and physicist, was the first to produce colloidal gold in 1857. He used phosphorus to reduce a solution of gold chloride (AuCl_4). This reducing agent causes the gold (Au^{3+}) ions to be reduced to neutral gold atoms, and slowly begin precipitating to form sub-nanometer particles. Faraday was also the first to recognize that the color of the gold was due to the extremely small particle size,⁴ and not that it was a gold-tin compound, as was previously believed.⁵⁻⁷

Faraday's colloidal gold is most likely the first monodispersed system ever reported in literature. Since then, interest in the preparation of monodispersed metal particles has only increased, mainly because of their superior performances as catalysts in many applications.⁸ The preparation of micrometer size metal particles was based on known techniques that have been well developed for both gold and silver.⁸⁻¹⁰ Two distinct methods have been developed: one involving the direct precipitation of particles from homogenous solutions using appropriate reducing agents, and the other involving the preparation of finely dispersed metal compounds, followed by conversion to metals of same shape through reduction in solution of gas phase. Here, the first scenario will serve as the basis for gold and silver microparticle formation. This nucleation and growth technique, developed by Matijevic and Goya, is reminiscent of the micron-sized silica particle synthesis pioneered by Stöber, Fink, and Bohn in 1968. They

produced monodispersed suspensions of silica spheres in the colloidal size range using the chemical reaction of tetraesters of silicic acid with certain solutions, such as methanol, ethanol, and n-propanol to produce silica.¹¹ Both techniques rely on initial reduction reaction rates to nucleate out a number of seed particles, which are then grown into the desired size.

Part II: Assembly

In the Velegol lab, a technique for fabricating complex colloidal assemblies has been established using particle lithography.¹² This technique provides a way to synthesize a localized functionalization of a particle. By adhering amidine polystyrene latex (PSL) particles, which are positively charged, to a negatively charged glass Petri dish surface, then adding a negatively charged polystyrene sulfonate to the particles, the entire surface of the PSL particles, except the part attached to the glass, becomes negative. The Petri dish is then sonicated to removed the adhered particles, which now contain a single positive region, and are considered lithographed.¹² Initially, these particles were added to a solution of negatively charged microspheres of silica in a 1:1 ratio, and the negatively charged particles bound electrostatically to the single positive region on the amidine PSL, which caused the formation of heterodoublets.¹²

The next step in the evolution of doublet formation involved the Velegol lab's "Salting out-Quenching- Fusing Technique." This technique, used to synthesize colloidal doublets, is based off of the concept that placing colloidal particles in a solution of high ionic strength will cause the particles to aggregate because of van der Waals forces.¹³ This is referred to as "salting out" the particles. By adding deionized water to dilute the ionic strength of the solution, the

aggregation of particles is quenched and no further aggregation occurs. The time at which this step should be taken is determined using the Smoluchowski rapid flocculation time, shown below.¹⁴

$$\tau = \frac{\pi \eta^3 \alpha}{2kT\phi}$$

where τ = Smoluchowski rapid flocculation time,

η = viscosity of the solution

α = radius of particles

ϕ = volume fraction of particles in solution

For the development of this technique, an estimate of the Smoluchowski rapid flocculation time was calculated to be on the order of seconds. However, because of the leftover gum arabic from the silver and gold synthesis, a process later described in the “Materials and Methods” section, aggregation was not seen for the system until much later, around 10 minutes.

Finally, the particles are fused together by using elevated temperatures. By heating the particles above their glass transition temperatures, the doublets permanently fused together by allowing the polymer chains of the touching particles to diffuse.¹⁵ Ultimately, the development of the “Salting out-Quenching-Fusing (SQF)” technique provides a quick and inexpensive way to fabricate colloidal doublets.¹⁵

The next phase of research performed to enhance the understanding of colloidal doublets focused on metallic colloidal doublets. The Velegol lab work focused on gold-gold, silver-silver, and gold-silver doublets of micrometer size. With these doublets, the fusing step of the SQF technique was not able to be used because of the high melting points involved with metal-metal doublets. Electrical connectivity was tested for using a hydrogen peroxide solution. When two spheres of the metallic doublet are connected in peroxide, a spontaneous autoelectrophoresis occurs in this system.¹⁶⁻¹⁸ This means that the difference in the catalytic ability of two metal particles (namely gold and silver) to break down peroxide caused the formation of a gradient of the half reaction products, one of which is the hydrogen ion. This results in a local electric field that causes the charged particles to move.

The techniques used to establish an assembly process for colloidal doublets also provided the foundation for this experiment's colloidal triplet assembly.

Part III: Applications

This work has goals in two main areas of application: photocatalysis and microrobotics. As a photocatalyst, this device has the potential to convert solar energy into a fuel source. High solar conversion efficiencies have already been shown to be achievable in a photoelectrochemical system using a silicon electrode with a platinum metal catalyst and an iodide redox electrolyte.¹⁸. Most processes of collecting solar energy convert it into a form of electrical energy and then into a storable chemical form. One goal of the cell designed in this experiment is to directly convert

solar energy into a storable chemical energy fuel. By circumventing an electrical form of energy, a fuel is created that can be stored and transported much more easily.

The catalytically generated electric field resulting from autoelectrophoresis, as described in the previous section, has been demonstrated on the macroscale to be able to induce an electroosmotic fluid flow that can be turned on and off externally when the circuit is completed or broken.¹⁷ This flow can drive an electrokinetic motor, and was successfully shown using a short circuit current between platinum and gold microelectrodes. When an insulator was inserted between the two metals, the flow stopped.¹⁷ The following set of experiments attempts to produce a similar effect for a colloidal triplet: by insertion of a semiconductor ‘valve,’ the motor can be turned ‘on’ or ‘off’ by changing the conductivity of this material.

Part IV: Research Problem and Hypothesis

Based on the science and experimental techniques described previously, my present research hypothesis is that a photoresponsive material can be assembled into a functional colloidal triplet assembly using manipulation of interparticle forces, surface modifications, and a variation of the SQF technique. The advances made relative to previous fabrication show that the processes used to produce metallic doublets can be extended to metallic-silicon-metallic triplets. For example, while controlled random aggregation is used for triplet formation, it must be made more specific. The successful assembly of this triplet also gives a foundation for further experiments that will be used to better control the rate of success of colloidal triplet formation.

Materials and Methods

Part I: Synthesis and Processing

To synthesize the gold particles, two 75 mL solutions were prepared. One contained 25 mM HAuCl_4 and 3 wt% gum arabic, and another contained 50 mM L-ascorbic acid and 3 wt% gum arabic. These solutions were stirred rapidly together for approximately two days in a 250 mL reaction flask. Upon completion of stirring, the gold particles settled for about three hours. The supernatant was drawn off and the gold particles were rinsed and resuspended in DI water. This process of drawing off the settling and drawing off the supernatant was performed twice.

The colloidal silver was formed using a similar procedure. Two solutions were again prepared, the first containing 167 mM of silver nitrate with 7 wt % gum arabic, and the second containing 333 mM L-ascorbic acid with 7 wt% gum arabic. These were combined, settled, and rinsed in the same manner as previously done with the gold particles.

To synthesize the silicon particles, silicon wafers from Sigma Aldrich were purchased. These wafers were broken into pieces and placed in a solution of acetone. The silicon was then crushed lightly using a mortar and pestle to reduce the size and suspend the resulting particles. In order to get the desired size distribution of 5-10 μm , the particles were filtered first with a 30 μm filter paper placed in a glass funnel to get rid of any overly large particles. They were then filtered again with 5-10 μm paper, and the residue was kept, resulting in a Si particle distribution of 5-30 μm , which was suspended in acetone (necessary for later functionalization).

Part II: Post Processing Functionalization

The silanizing agent, used to surface-modify the silicon, was aminopropyl-triethoxysilane. This agent chemically bonds to the 2 nm thick native oxide layer that forms on silicon, and remains stable even after sonication.

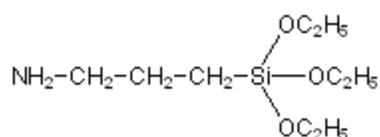


Figure 1: Structure of 3-aminopropyltriethoxysilane

In this reaction, traces of water in acetone react with 3-aminopropyltriethoxysilane, which becomes activated and bonds to the oxide layer on the silicon surface, forming a very stable siloxane (O-Si-O) bond. After the 3-aminopropyltriethoxysilane was added, the supernatant solution was removed from the petri dish, and fresh acetone was added. This was performed three times, allowing the silicon to settle each time before removing the supernatant solution and adding fresh acetone. The newly silanized silicon was dried completely on a petri dish, which was scraped off and placed in a small amount of water for use in the assembly process.

Part III: Assembly of Photoactive Chemical Cell

The triplet photoactive chemical cell was formed by using the salting out-quenching technique described in the introduction. The gold and silver stock solutions that were created had volume fractions of .000216 and .000646, respectively. The radius of each gold particle is much smaller than that of silver, with gold particles having a diameter of approximately one μm , and silver

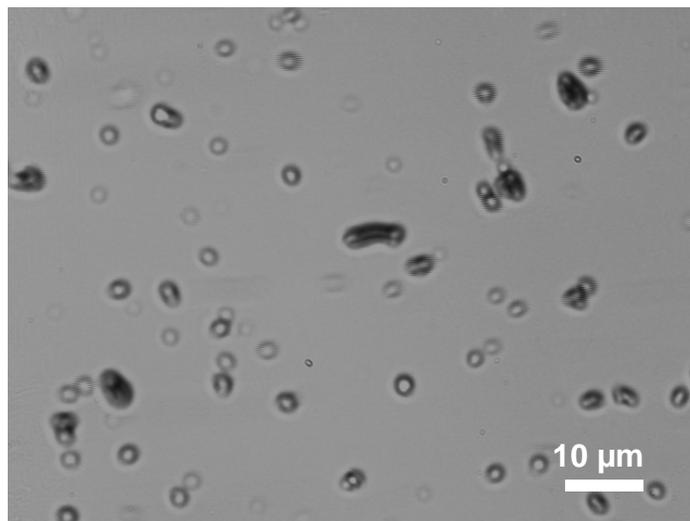
approximately 2 μm . Because of this, the volume fraction must in turn be smaller with gold to compensate and make the actual number of particles approximately equal. The volume fraction of silicon in the prepared solution was approximately .000152.

A monolayer of gold was settled onto the surface of the petri dish and 1 M KCl was added, which caused the gold to stick to the glass. The petri dish was then rinsed 10 times to remove all KCl and excess gold. Next, a monolayer of amino-silanized silicon was added to the gold monolayer, and was allowed a settling time of 10 to 15 minutes, after which all of the large silicon had settled to the monolayer of gold. The silicon particles adhered to the gold through electrostatic attractive and van der Waals forces. The petri dish was rinsed two times to remove the unstuck silicon. A monolayer of silver was then added, settled, and the petri dish was rinsed 5 more times to remove the excess and unstuck silver from the solution. The silver particles preferentially stick to the silicon particles, and not to the gold, due to the electrostatic forces between all three particles.

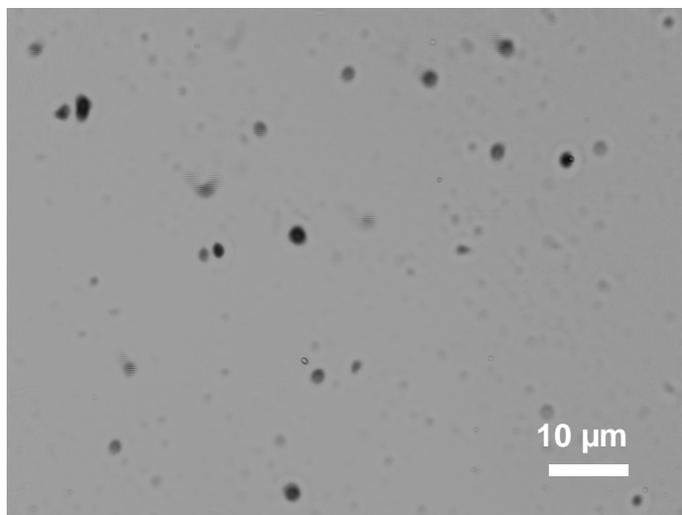
After thoroughly rinsing the particles, they were then scraped off using a stainless steel micro spatula and examined. Images were used to analyze the process at each stage, as well as to determine whether the trimer assembly was achieved as an end result.

Results and Discussion

The following optical images were taken using a Nikon Eclipse TE2000-U inverted optical microscope with magnifications of 20, 40, 60 and 100x. Detailed images were obtained using JEOL 6700F field emission scanning electron microscope (FESEM) with accelerating voltages of 3 and 5 keV and an operating current of 20 μ A, allowing for magnifications from 1300 to 150000x. All images depict the process of assembling the photoactive colloid as well as the successful creation of the final structure.

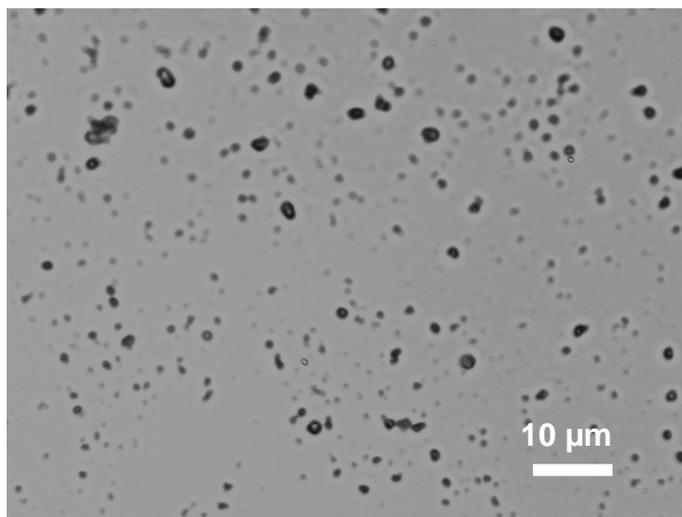


**Figure 2: Crushed silicon particles before first filtration.
(Imaged by Golden)**



**Figure 3: Crushed silicon particles after third filtration
(Imaged by Golden)**

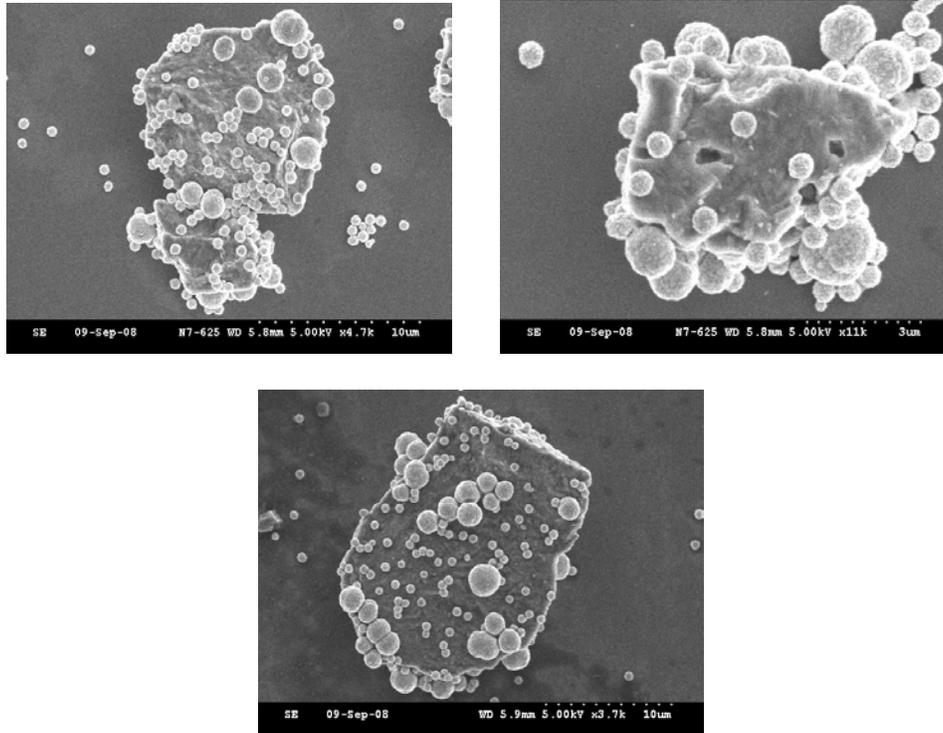
A comparison of figures 2 and 3 shows the effectiveness of each successive filtration of the crushed silicon particles. Initially, the particles are larger and more varied in size after being crushed with a mortar and pestil. After three filtrations using filter paper, the remaining particles were of appropriate size for the trimer structure (5-30 μm).



**Figure 4: Silicon after gold and silver were added
(Imaged by Golden)**

Figure 4 shows that while many silicon particles are present in the solution, free gold and silver

particles are also interspersed. This may lead to further unwanted aggregation after assembly. Additionally, it is difficult to determine what (if any) gold and silver particles are present on the silicon using optical microscopy. Thus, SEM images were taken to determine the final configurations of the silicon particles.



Figures 5-7: Gold and silver particles aggregating on silicon surface (Imaged by McDermott. Scale bar in lower right corner of each image)

Figures 5-7 illustrates the most common formation resulting from these experiments. Gold and silver particles successfully attached to silicon, but also aggregated on the surface. Note that gold particles are visibly smaller than the silver. Ideally, only one gold and one silver particle should be on the surface of each silicon particle. In the future, altering the surface coverage of the gold and silver, the size of the silicon, and finding a way to prevent further aggregation are all important considerations that should be examined to improve this final structure.

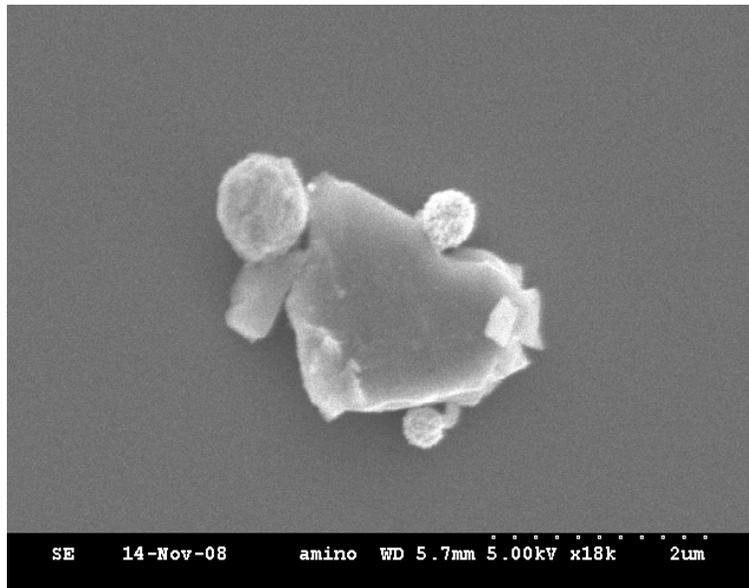


Figure 8: Successful Assembly
(Imaged by McDermott. Scale bar in lower right corner of image)

Figure 8 demonstrates a final successful assembly of one gold and one silver particle attaching to the silicon surface without touching any other gold or silver particles. This was the only successful structure in multiple images, suggesting that a separations step will need to be added for successful completion of this work.

Conclusion

This thesis work has led to the successful assembly of the colloidal triplet structure, and is a major step forward in the ultimate goal of a photoactive colloid triplet that will successfully run a reaction to generate a storable form of energy. The next step in optimizing the assembly process will be to improve the control of the process and produce a greater proportion of triplets formed in solution. This will involve further experimentation on aggregation time, different materials used to form the trimer, and different methods of surface functionalization.

This research was completed in the Spring of 2009. Since then, the Quenched Electrostatic Aggregation (QEA) technique, used to assemble colloidal trimers out of two or three different materials, has been developed. Understanding both the role that electrostatic interactions play in assembling particles and the importance of halting further aggregation has directly led to the QEA technique.

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