Volumetric Size Control on the Photoinduced Synthesis of Silver Triangular Nanoprisms

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Abstract

The effects of volumetric size-control techniques on the photoinduced conversion of silver colloids to triangular nanoprisms were examined. It was hoped that through the application of size-control techniques on photocatalyzed reactions, a new method of controlling particle dimensions could be established. Initial work focused on optimizing the synthesis procedure in order to obtain efficient photoconversion to the desired product in the bulk. Despite considerable challenges at this step of the investigation, a generally successful synthetic procedure was developed. This conversion process was then carried over into micrometer-scale hemispherical wells in order to impose control through volumetric restriction. Ultimately, difficulties with solvent evaporation and reaction byproducts inhibited the conversion reaction. A second reactive scheme for the development of silver triangular nanoprisms was investigated as an alternative, but unpredictable reactive products limited its use in a volumetric size control scheme.

Introduction

Currently there is much research on the development of the tools and techniques of nanotechnology. Just as carpenters rely on their tools and skills to produce their products, so too will the nanoengineers of tomorrow rely on a wide array of synthetic strategies to make advancements possible. One category of synthetic reactions, that of photoreactive or light-catalyzed synthetic processes, is vital in relation to many of the nanoscale fabrication techniques currently being explored. The combination of photoinduced synthesis and nanoscale techniques of volumetric size control could add a new dimension to the synthesis of photoreactive materials.

Past research on the synthesis of photoreactive particles in the bulk generally examined ways of controlling reactive products through such variables as the wavelength and intensity of light used, the concentration of reactants in solution, or the addition or omission of certain reactive agents.[1,2,3,4] Though these methods of controlling photoinduced reactions are known, for the most part reactions progress without the fine level of control necessary to develop nanotechnologically significant materials. To better control these reactions, volumetric size control may be applied. In this process the reaction volume itself is limited to extremely small scales in order to regulate the quantity of reactants available and limit the dimensions of product materials.

This research examined the interplay between photocatalyzed reactions and volumetric size-control techniques. Because the reaction studied — the conversion of silver colloids in solution to triangular nanoprisms — produces anisotropic particles, other lines of investigation become available: Will these triangular prisms have a preferred orientation, such as alignment in stacks, or will their placement be purely random? Can this alignment be affected by modifying the dimensions of the volumetric structure itself? Due to limitations in reactants available, will the growth of the particle be favored in one particular dimension, such as width over height? These questions, and many more, present themselves as this new dimension of control through volumetric limitation is exerted over the photoinduced synthesis of silver triangular nanoprisms.

Figure 1: Bulk silver colloid after exposure for up to 15 days.

Background

Silver is of interest in nanotechnology research because of its interesting optical and electronic properties and quantum confinement at the nanoscale level. A wide variety of nanoscale silver structures have been synthesized, such as belts, plates, colloids, and, recently, triangular nanoprisms.[1,2,3,4,5] The conversion of solution-phase silver colloids of a diameter of less than 10 nm into triangular nanoprisms with an approximate edge length of 70 nm is the object of the investigation described here.[5,6]
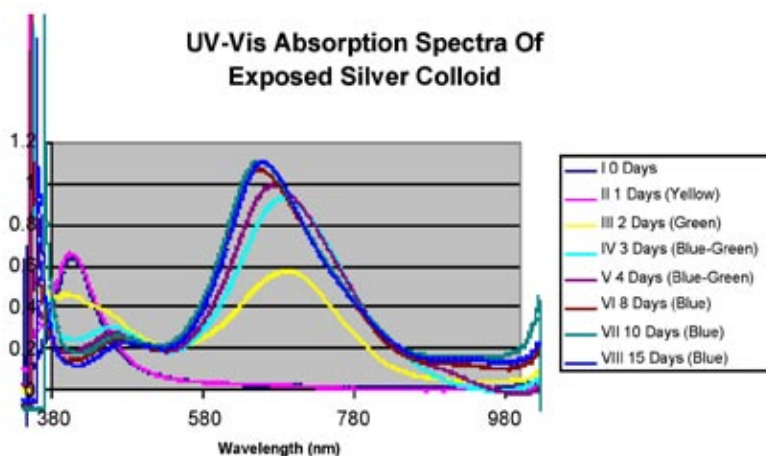
Figure 2: UV-Vis absorption spectra of bulk silver colloid after exposure for up to 15 days.
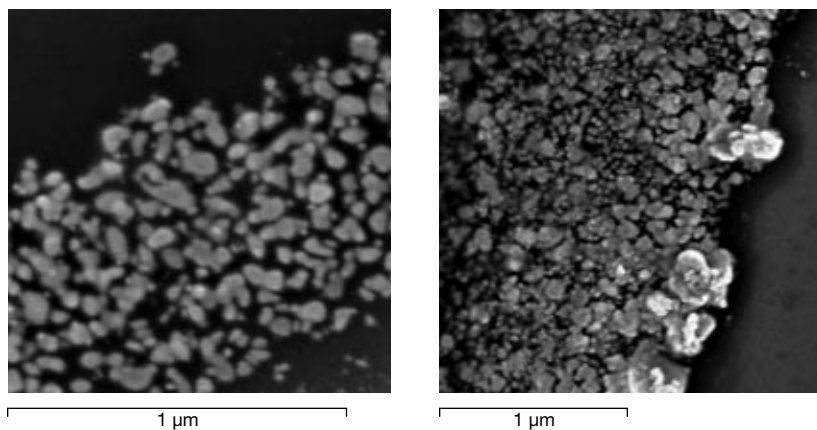

Figure 3: SEM image of reaction products after exposure for two days (a green solution).

Figure 4: SEM image of reaction products after exposure for four days (a blue solution).

Past research has shown that the edge length of synthesized triangular nanoprisms can be controlled through the wavelength of light used to induce the reaction. It has been proposed that the mechanism of control involves the production of different plasmon resonances, or harmonic oscillations of the electron densities, from different wavelengths of light.[5,6] These plasmon resonances not only direct the formation of the initial 70 nm edge silver nanoprism, but the presence or absence of particular frequencies also determines whether a secondary reaction occurs, in which four 70 nm edge nanoprisms combine to produce one 150 nm edge triangular nanoprism. The progress of this reaction can be monitored, both visually and using UV-Vis spectroscopy, as the solution changes from a yellow colloid to a dark blue solution.[5,6]

Recently a second synthetic scheme has been developed for the synthesis of silver triangular nanoprisms. This one no longer relies on light to induce the reaction, but uses thermodynamic means in a bulk phase solution.[7] Though some control over edge length is lost, much greater influence may be exerted over the thickness of the nanoprisms simply by varying the concentration of one reactant, sodium borohydride. This synthetic route lacks the photoreactivity aspect of the other type of reaction, but it offers the possibility of a reactive scheme that may be controlled through micro- and nanoscale volumetric techniques.
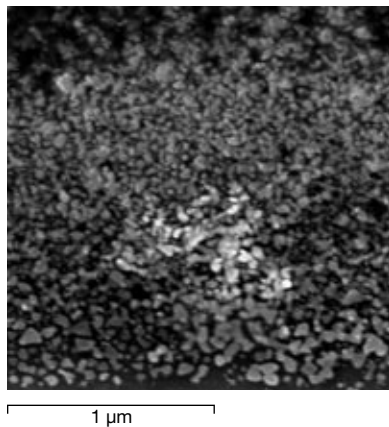
1 μm

1 μm

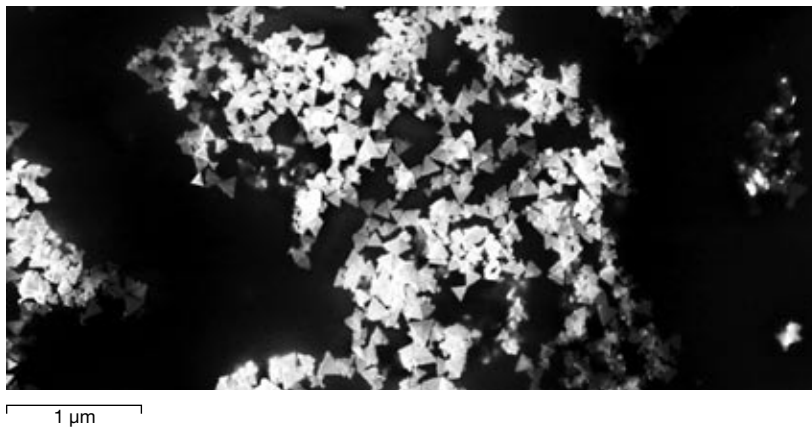**Figure 5: SEM image of reaction products after exposure for eight days (a blue solution).**

Figure 6: SEM image of reaction products after exposure for 15 days (a blue solution). Silver triangular nanoprisms of two distinct sizes are clearly visible.

Approach

A dependable method to produce precursor silver colloids needed to be established. These synthesized colloids must be tested for their ability to produce silver triangular nanoprisms. This is done by exposing bulk samples to the conditions that will exist in the conversion of the volumetrically controlled samples, with the reaction's progress monitored by observing color change and using UV-Vis spectroscopy.

Once a viable synthetic production method was established, volumetric size control of the photoinduced reaction would be applied. This is done by introducing the precursor colloid solution into microscale structural arrays — in this case, 3-micrometer hemispherical wells in polydimethylsiloxane (PDMS) — through discontinuous dewetting. Samples are then exposed to a light source to induce the conversion reaction in the microscale wells. Since the reaction requires a solution-phase environment

and involves small volumes of solvent, the added complication of solvent evaporation becomes a primary concern. A variety of preventative measures must be taken, including the capping of the well arrays with an additional piece of PDMS, as well as having the conversion occur in a humid atmosphere. Once the conversion has taken place, the products can be analyzed initially through dark field (DF) optical microscopy and conclusively through scanning electron microscopy (SEM).

The investigation also focused on the thermal synthesis of silver nanoprisms. It was hoped that this secondary reaction could also be subjected to volumetric size control in order to influence the properties of the product particles. To test this, the reactive silver colloid solution was ttransferred into the same 3-micrometer well arrays used previously and allowed to convert into nanoprisms, which would be analyzed through DF optical microscopy and SEM.

Results and Discussion

Of the reaction ratios explored, the following reaction scheme was most successful at creating silver colloids that would convert efficiently. In a typical synthesis, freshly prepared aqueous solutions of silver nitrate (40 mM, .25 mL) and trisodium citrate (30 mM, 1 mL) were added to 95 milliliters of millipure water. This solution was stirred vigorously for 15 min at room temperature, at which point a chilled and freshly prepared aqueous solution of sodium borohydride (16.6 mM, .3 mL) was quickly added. Concurrent with the addition of the sodium borohydride, an aqueous solution of (BSPP) bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (10 mM, 1 mL) was added dropwise over approximately 5 min. Immediately after the addition of the sodium borohydride reducing agent, the solution was observed to turn a light golden color. This reaction solution was then allowed to stir for an additional

30–45 min, during which time the light yellow color changed to a much richer, golden yellow.

Though the described synthetic processes were successful most of the time, there were unexplained failures. Even though the same synthesis was in use, at times the reactions failed to produce a satisfactory colloidal solution; in some cased the silver reduced too quickly and crashed out of solution to form a jet-black powder. The causes for these failures in the reaction are not clear, but contamination in the reaction vessels or of the reactants themselves is possibly to blame.

Once the precursor silver colloids had been synthesized, they were exposed to visible light in order to produce silver triangular nanoprisms in the bulk. Samples were placed in glass vials, sealed, and then exposed to ambient fluorescent lighting. Over approximately 15 days, the initial dark yellow color was observed to change to a light green, then aqua green, followed by light blue, and finally resting at a dark blue color (Figure 1). During exposure, samples were subjected to UV-Vis spectroscopic analysis. UV-Vis spectra clearly indicated the decrease in the initial silver colloid absorbance peak, located at 412 nm, and the development of the characteristic silver triangular nanoprism peak at approximately 665 nm (Figure 2). The exact position of this nanoprism peak seemed unstable, tending to emerge at approximately 710 nm before finally blue shifting to its final location. The cause of this transition is unclear, but the rounding of the nanoprism tips over time may have been a factor.
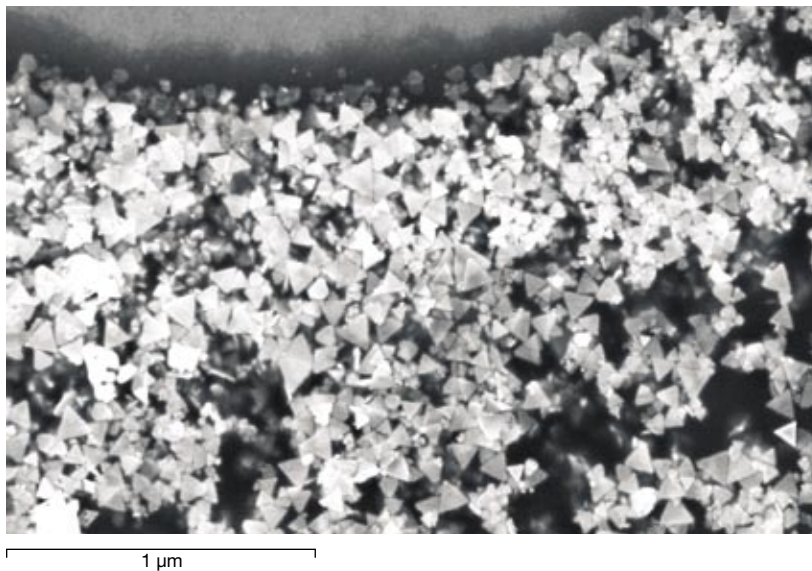

1 μm

Figure 7: SEM image of reaction products after an exposure time of 15 days (a blue solution). Silver triangular nanoprisms of two general edge-length ranges can be seen (approximately 90 nm and 180 nm).
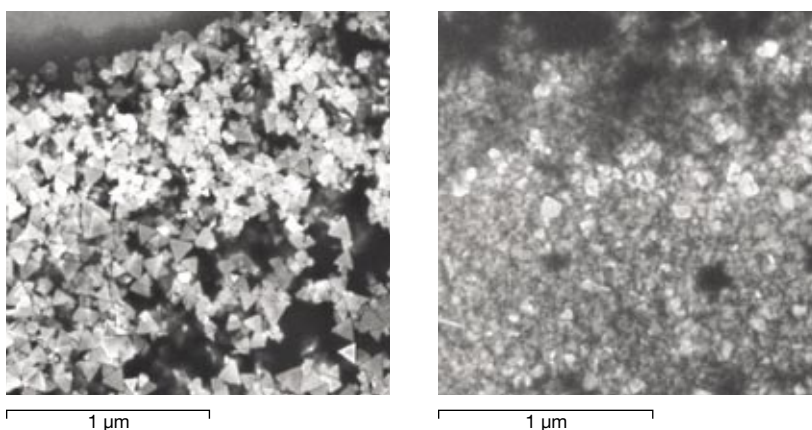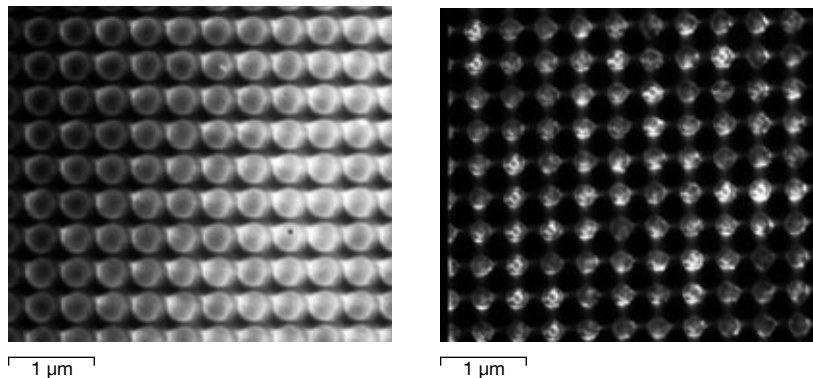

1 μm   1 μm

Figure 8: Successful (left) and failed (right) conversion reactions. The same colloidal solution was used in both instances and exposed for equivalent amounts of time (15 days), but were separated by a period of four months.

1 µm

1 µm

Samples of this developing solution were also examined using scanning electron microscopy (SEM), which showed the final product to be a mix of triangular nanoprisms of approximate edge lengths of 90 nm and 180 nm (Figures 3–7). At each of the intermediate steps, conversion products tended to be primarily composed of amorphous particles of approximately analogous dimensions as the final products. Desired reactive products also tended to be accompanied by much larger amorphous particles and films, most likely conglomerations of reactive byproducts. These unwanted contaminants must be removed in order to study the isolated synthesized nanoparticles, but an efficient purification method wasn't available because the requisite colloidal size was maintained through the bonding of organic ligands to the surface of the particles. Attempts to remove these organic byproducts, such as by organic extraction, would result in the loss of these stabilizing ligands and the decay in the structure of the product particles.

Another problem arose in the initial study of the conversion in the bulk. Past investigation into this synthesis yielded converted particles in approximately 70 hours,5 but conversions in this

investigation took considerably longer, often up to 15 days. The cause of such a lengthening of the conversion time was unclear, but it is possible that either the ambient light used was less intense than that used in prior examinations, or that there may be an unidentified aspect to the precursor colloidal solution that determines conversion time. What is clear is that in order for this reaction to be used efficiently in micro- and nanoscale structures, the conversion time must be shortened significantly.

One point of interest is that even though the solution color visible changed very little once it had achieved a dark blue color, the structure of the product nanoprisms continued to undergo vast changes. Monitoring of the reaction progress was problematic since the visible color of the solution does not necessarily confirm the quality of the product particles. This discrepancy also was present in the UV-Vis spectra, which showed absorption peaks in the region thought to be indicative of the presence of triangular nanoprisms despite the fact that only the amorphous particles were dominant (Figure 2). In some cases, colloidal samples that had previously converted successfully failed to convert

to the desired product (Figure 8). This failure may indicate that photoinduced conversion of colloidal samples is possible only within a limited time.

Despite the complications, samples were then prepared by injecting the colloidal precursor into arrays of 3-micrometer diameter wells in PDMS through discontinuous dewetting. The samples were then sealed with PDMS slabs and placed above aqueous reservoirs to prevent solvent evaporation during the conversion process. It was found that the oxidation of both the array and capping PDMS, of times 30 and 15 sec respectively, helped to greatly increase the hydrophillicity of the PDMS and aid in the dewetting process. Samples were then exposed and the conversion process monitored by UV-Vis spectroscopy of bulk control samples exposed to the same conditions. Once the conversion had terminated, as evident by characteristic UV-Vis absorption spectra, the samples were removed from the light source and analyzed by dark field optical microscopy (Figure 9), in order to indicate the presence of particles in the wells, and finally by SEM to further identify the nature of these particles (Figures 10–11).
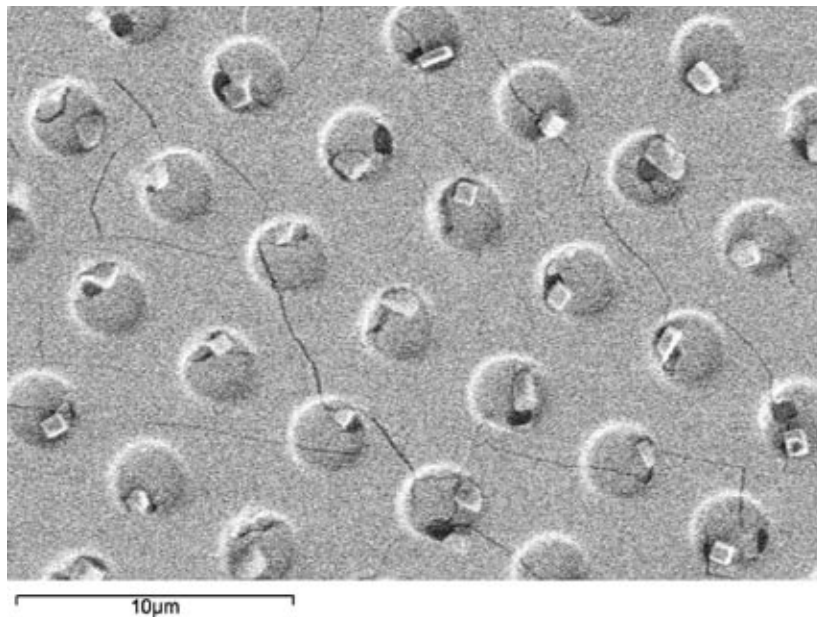
Figure 10: SEM image of converted products in 3-micrometer well arrays. Large crystalline products indicated the failure of the photoinduced conversion reaction and the possible presence of recrystallized reaction by-product.
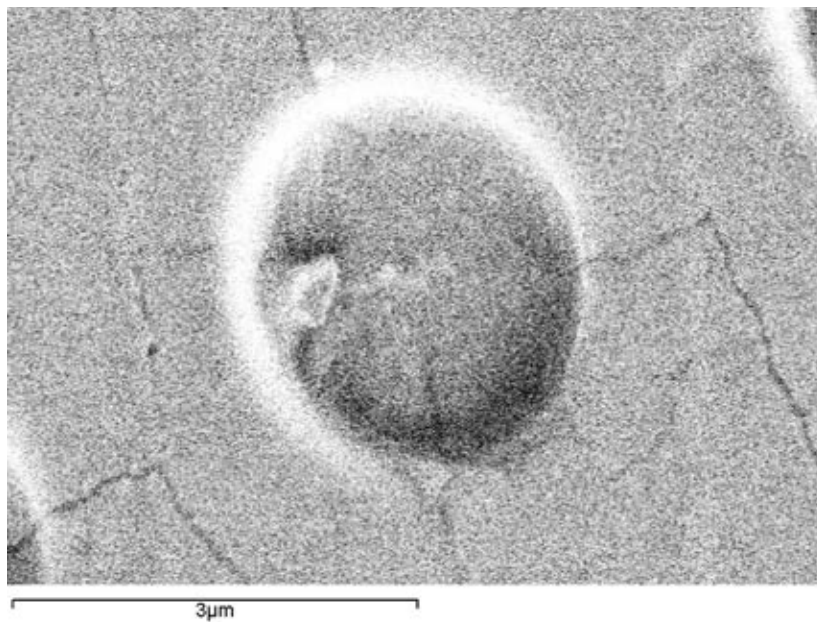

Figure 11: Close-up SEM image of a 3-micrometer well in PDMS.

Dark field imaging revealed the presence of several particles in the well arrays, indicating that the discontinuous dewetting had successfully deposited the reactive precursor colloid in the wells. SEM revealed that the particles developed in the wells were not the targeted silver triangular nanoprisms, but most likely crystalline formations of reaction byproducts that remained in solution; none of the wells displayed any of the desired nanoprism products. One possible explanation is that premature evaporation of the solvent caused the recrystallization of the reactive byproducts, as well as the unwanted termination of the colloid conversion process. This failure points to the importance of maintaining the aqueous environment that is crucial for the reaction process to occur.

In light of the difficulties with the photo induced conversion process as applied to the proposed volumetric size-control mechanism, the possible thermal synthesis of triangular nanoprisms was also examined. A variety of synthetic schemes were attempted, but no clear, effective method presented itself. Previous work substituted poly(vinylpyrolidone) for BSPP, but the reactions attempted here used BSPP, which was indicated as acceptable by the literature.[7] Reaction outcomes tended to be sporadic at best, but they followed the general scheme given in the literature: the reactants were added, and after approximately 30 min the solution would flash a series of colors before finally either reverting to a yellow colloid color, becoming overly reduced and black in color, or becoming clear all together. Of the few syntheses which produced products of stable color, SEM imaging revealed only large amorphous particles in the solution.

Even more curious is the fact that identical reaction processes would often yield different results. It is possible that BSPP may not be substituted for PVP as effectively as indicated by past work, or that subtle variations in reactant addition timing produced a wide range of outcomes. What is clear is that in its current state the thermal synthesis of triangular nanoprisms is unpredictable, and the conversion process occurs far too rapidly to be effective for use in the volumetric size-control investigation.

Conclusions

For future investigations into the volumetric size control of the photo-induced synthesis of silver triangular nanoprisms to proceed, several obstacles must be overcome. Most importantly, the conversion time necessary to produce nanoprisms must be reduced. This reduction would alleviate complications in the reaction due to solvent evaporation. The discrepancy between the visible solution color, the UV-Vis absorbance spectra, and the actual progression of the reaction also must be resolved in order to efficiently monitor the conversion process. It would be beneficial to investigate possible purification techniques in order to remove as much of the reactive byproducts in solution as possible, ideally with the result of preventing the formation of large agglomerates as observed in this investigation. Finally, to achieve a dependable conversion process, the sources of the seemingly random failure in the conversion and colloidal synthesis steps must also be identified and eliminated.

The investigation revealed several difficulties with the reaction of interest, but it also demonstrated several principles important to the field of nanoscale fabrication. The use of discontinuous dewetting to deposit sample solution into the structures worked effectively. The colloid synthesis reaction was also investigated in great depth so that future work might easily carry it over into nanoscale structures using an optimized reaction scheme. Many of the conditions for the success of the conversion reaction were also identified, which will prove invaluable for future studies. Using the advancements of this investigation, and once certain crucial flaws have been eliminated, future research will be able to advance the study of the interaction between volumetric size-control techniques and photoinduced reaction products.

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