

Synthesis and Characterization of Size- and Shape-Specific Gold Nanocrystals for Superlattice Assembly

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Abstract:

In this work, gold nanoparticles of different shapes and sizes were systematically synthesized, characterized, and assembled. The best control over their size distribution and morphology was achieved using seed-mediated growth. By varying reaction and sample preparation conditions, gold nanocrystal (AuNC) growth was directed into various shapes. These nanocrystals were characterized using UV-vis spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to determine final shapes and packing structures. The amount of free ligand in solution and the concentration of seeds used in the growth solution resulted in visible differences in both nanocrystal morphology and their packing assemblies. Sample preparation conditions, including drying temperature, drying speed, and droplet orientation, were also investigated. By successfully controlling reaction parameters and sample preparation conditions, it is possible to synthesize uniform, ordered structures with tailored shape- and size-specific properties.

Introduction:

Colloidal AuNCs have many applications in optical [2] and medical sensing, and when assembled into collective structures, their properties are even further tunable. In this work, AuNCs were synthesized and assembled into close-packed structures.

Experimental Procedure:

Size- and shape-specific gold nanocrystals were fabricated using seed-mediated growth [4], which involved making aqueous seed solutions and growth solutions separately. By exploring parameters involved in synthesis and preparation, we hoped to achieve ordered, close-packed structures of AuNCs by producing crystals with monodisperse shape and size.

Seed Solution Preparation. A 10 mL aqueous solution of 2.5×10^{-4} M hydrogen tetrachloroaurate trihydrate (HAuCl_4) and 0.10 M cetyltrimethylammonium chloride (CTAC) was prepared. Next, a cold, 10 mL aqueous solution of sodium borohydride (NaBH_4) was prepared. When ready, 45 μL of the NaBH_4 solution was added to the HAuCl_4 solution and allowed to stir for two minutes to initiate nucleation of AuNC seeds. The solution was then aged for at least one hour at 30°C.

Growth Solution Preparation. Multiple aqueous growth solutions were prepared (10 mL total volume). The synthesis of two shapes of gold nanocrystals (cubes and rhombic dodecahedra) were targeted. To direct the nanocrystal shape, different amounts of ascorbic acid (the shape-directing agent) were added. All reagent volumes

in the growth solutions were kept constant (0.32 g CTAC, 250 μL stock HAuCl_4 , and 10 μL of 0.01 M NaBr solution) except for the water and ascorbic acid. For cubic shapes, 9.625 mL deionized water and 90 μL ascorbic acid were added to the other reagents in the vials; for rhombic dodecahedral shapes, 9.565 mL deionized water and 150 μL ascorbic acid were added.

Directing the AuNC Size. To tune the nanocrystal size, the volume of seed solution added to the growth solutions was varied. For each target shape (cubes and rhombic dodecahedra), three different nanocrystal sizes were prepared by adding 25 μL , 45 μL , and 100 μL of seed solution to the growth solutions.

Purification and Deposition. The final solutions were purified via centrifugation, and droplets of the different solutions were deposited onto silicon wafers. Cleanliness of solution, drying temperature, and evaporation rate all affected the AuNC assembly process and SEM image quality.

Results and Conclusions:

The AuNCs displayed a clear size trend, depending on the volume of seed solution that was added to the growth solution, as shown in Figure 1. As the number of seeds added to the growth solution increased, final nanocrystal size decreased, and vice versa. This is because if larger quantities of seed are added to a growth solution, there is less growth reagent available per seed, resulting in smaller crystals.

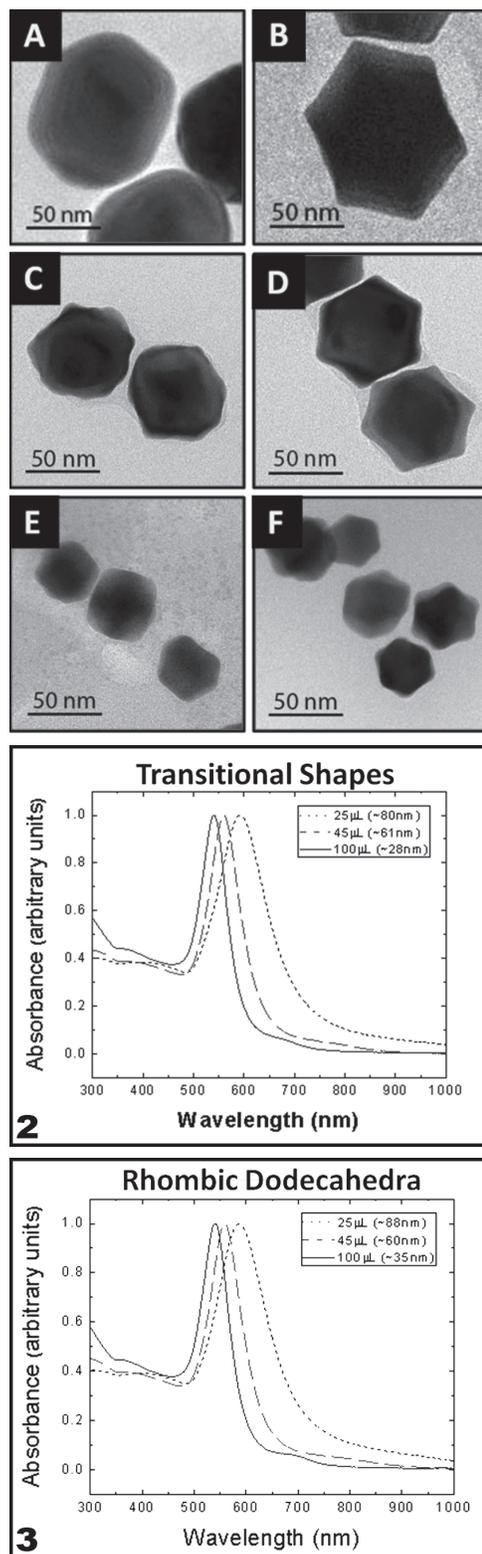


Figure 1, top: AuNCs with different volumes of seed solution added. Left column: Transitional shapes; A) 25 μL , C) 45 μL , E) 100 μL . Right column: Rhombic dodecahedra; B) 25 μL , D) 45 μL , F) 100 μL . **Figure 2, middle:** The largest size AuNC (80 nm) has the plasmon band furthest in the infrared because its electrons oscillate at a longer wavelength than smaller size AuNCs. **Figure 3, bottom:** A similar trend in plasmon frequency is seen here with a red-shift in peak position as the AuNC increases in size.

In Figures 2 and 3, there is shown a clear trend between the optical properties of the AuNCs and their size. Since gold is a plasmonic material, different AuNC diameters resulted in different plasmon bands (the peaks in the graphs). This is because the electrons in the particles oscillated collectively at different frequencies for particles with different dimensions [2].

Although rhombic dodecahedral nanocrystals were synthesized successfully, the cubic shapes that were targeted more closely resembled a transitional shape somewhere between a cube and a rhombic dodecahedron. Figure 4 displays several of the close-packed assemblies that were achieved. It is evident that the size and shape monodispersity of the AuNCs was the most important factor in achieving well-ordered structures.

Future Work:

With greater control over AuNC size and shape, it is possible to assemble them into chains, 2D superlattices, and 3D supercrystals. These structures enable a variety of applications in metamaterials [2], optical sensors, and acoustic wave sensors [1], due to their collective plasmonic properties [3] when assembled into ordered supercrystals.

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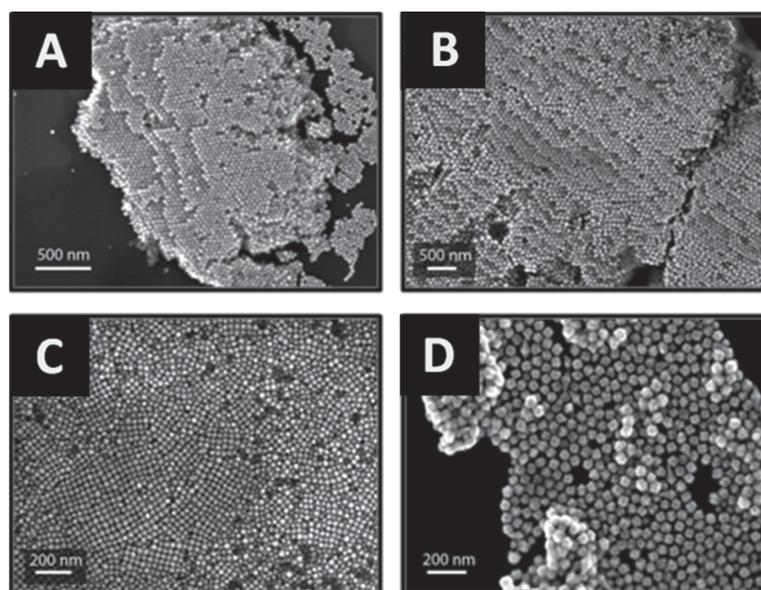


Figure 4: Some of the most closely-packed AuNC structures achieved under various conditions. Well-ordered structures occurred largely because of the monodispersity of the crystals within the sample.