

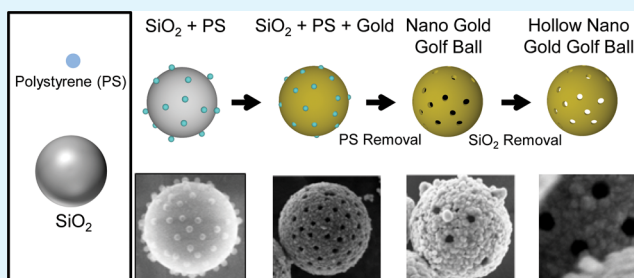
## Designing Hollow Nano Gold Golf Balls

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**ABSTRACT:** Hollow/porous nanoparticles, including nanocarriers, nanoshells, and mesoporous materials have applications in catalysis, photonics, biosensing, and delivery of theranostic agents. Using a hierarchical template synthesis scheme, we have synthesized a nanocarrier mimicking a golf ball, consisting of (i) solid silica core with a pitted gold surface and (ii) a hollow/porous gold shell without silica. The template consisted of 100 nm polystyrene beads attached to a larger silica core. Selective gold plating of the core followed by removal of the polystyrene beads produced a golf ball-like nanostructure with 100 nm pits. Dissolution of the silica core produced a hollow/porous golf ball-like nanostructure.

**KEYWORDS:** hollow, porous, nanocarrier, gold shell, template, hierarchical



Porous and hollow/porous nanostructures of various materials with sizes ranging from 100 nm to 100  $\mu\text{m}$  are of current interest in catalysis,<sup>1</sup> photonics,<sup>2</sup> biosensing,<sup>3</sup> nanodelivery,<sup>4,5</sup> cell culture,<sup>6,7</sup> and toxin scavenging.<sup>8</sup> The unique properties of nanostructured gold are of current interest. Hollow/porous particles made of gold are desirable because of gold's surface plasmon resonance<sup>9</sup> and use in surface enhanced Raman spectroscopy.<sup>10</sup> Gold is relatively biocompatible and can be chemically modified using a variety of moieties. Gold has been the material of choice in the fabrication of many nanostructures including spheres,<sup>11</sup> rods,<sup>12</sup> core/shell structures,<sup>13–15</sup> assembled vesicles,<sup>16</sup> and spiky gold shells.<sup>17</sup> However, particle diameter and pore size determine many potential applications of the particle and control of these two features has been difficult.

Over a decade ago, a variety of different approaches were employed to fabricate large, porous gold nanostructures. One previous approach filled the voids of a colloidal crystal template with colloidal gold and sintered the gold together prior to removal of the template.<sup>18,19</sup> A different approach used colloidal gold and emulsion-templated polymers to fabricate macroporous gold beads with diameters ranging from 0.5–1 mm.<sup>20</sup> Another approach filled the matrix in porous polystyrene spheres with colloidal gold. Subsequent removal of the polystyrene by calcination resulted in macroporous porous gold spheres with diameters  $\sim 9 \mu\text{m}$ .<sup>19</sup> The latter two synthesis processes could perhaps be scaled down to produce particles with smaller diameters; however, it remains to be demonstrated.

In the past decade, several routes leading to the realization of hollow/porous gold particles have emerged. These routes have

offered better control over particle diameter and pore size. One notable route employed electroless plating to grow a silver shell on top of a previously grown gold shell on a spherical polystyrene core.<sup>21</sup> The particles then underwent a calcination process which alloyed the gold to the silver and decomposed the polystyrene. This was followed by acid etching of the silver from the shells. The removed silver resulted in a restructuring of the gold atoms in the shell creating nanoporous rifts throughout most of gold the shell.<sup>21</sup>

Recently, a technique for creating colloidal hierarchical templates has emerged. These templates consist of a core particle with smaller satellite particles attached to it. A shell is then selectively grown on the exposed surface of the core particle. Removal of the template results in shells containing pores with a morphology defined by the shape of the attached satellite particles. Colloidal hierarchical templates have been used (by Zhao and Collinson) to fabricate porous gold shells.<sup>22</sup> Also, Wan et al. used the process to create nanosized colloidal hollow/porous silica shells.<sup>23</sup>

Previous synthesis processes employing colloidal hierarchical templates used the same material for the satellite and core particles.<sup>22,23</sup> In this work, we extend the hierarchical template strategy by using different core (silica) and satellite (polystyrene) materials to create two different types of particles (core–shell golf balls and hollow gold golf balls). We demonstrate the process is also size scalable by using cores

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with diameters of 200 and 1000 nm. We also present the effect of different gold plating conditions on the morphology of the gold shells formed.

Colloidal polystyrene spheres with carboxylate-modified surfaces (2.73 wt % in water) with 100 nm diameters, spherical colloidal silica with 200 and 1000 nm diameters (prepared as 2 wt % in water); poly(diallyldimethylammonium chloride) (PDDA,  $M_w \sim 8,500$ ) were purchased from PolySciences. Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80% solution in water), and sodium hydroxide (NaOH, 10 M) were purchased from Aldrich. Potassium carbonate ( $K_2CO_3$ ), formaldehyde (37%), ammonium hydroxide ( $NH_4OH$ , 29%), and hydrofluoric acid (HF, 48%) were purchased from Fisher Scientific. Dimethylformamide (DMF) was purchased from Macron Chemicals. Anhydrous ethyl alcohol (EtOH) was purchased from JT Baker. Chloroauric acid ( $HAuCl_4$ ) was purchased from Sigma and prepared as a 1 wt % solution in water. The water used in all experiments was produced using a Millipore Advantage A10 system with a resistance of 18.2 M $\Omega$ .

Colloidal silica has a net negative surface charge at pH values above 2.2. The net charge on the surface of colloidal silica can be reversed using a cationic polyelectrolyte such as PDDA.<sup>24,25</sup> This was performed by adding 320  $\mu$ L of ammonium hydroxide to 5 mL of 2 wt % dispersions of colloidal silica (pH  $\geq 11$ ). Subsequently, the solution was placed in an ultrasonic ice bath at 4  $^\circ$ C, and then 5 mL of 1 wt % aqueous PDDA solution was added into the mixture. The resulting solution was left in the ultrasonic bath for 20 min. The tube containing the solution was then centrifuged at 3200 g for 10 min to remove unadsorbed polymer. Centrifugation and redispersion was repeated four times and transferred to a clean container. On the final rinse the silica was redispersed in 5 mL of water.

Carboxylate-modified polystyrene spheres with 100 nm diameters were electrostatically attracted to the 1000 nm PDDA-functionalized silica as follows. In a 2 mL centrifuge tube, 1 mL of the PDDA-functionalized silica was centrifuged at 3200 g and redispersed in 1 mL of EtOH. The tube containing PDDA-functionalized silica solution was placed in an ultrasonic ice bath at 4  $^\circ$ C for 10 min. Then 25  $\mu$ L of aqueous carboxylate-modified colloidal polystyrene was added to the PDDA-functionalized silica and left in the ultrasonic ice bath for an additional 5 min. The mixture was then centrifuged at 1000 g for 5 min, decanted and the pellet was redispersed in 1 mL of water.

Colloidal gold nanoparticles with  $\sim 3$  nm diameters were used as seeds for the gold plating process.<sup>26,27</sup> The utility of the colloidal gold seeding solution was dependent on the order and method by which the reactants were mixed during their synthesis.<sup>26</sup> They were prepared by mixing 54 mL of water and 50  $\mu$ L of 10 M sodium hydroxide together. In a separate container 12  $\mu$ L of 80% THPC was diluted in 1 mL of water and aged for 5 min before being added to the aqueous sodium hydroxide solution. The mixture was stirring for an additional 5 min prior to the addition of 2 mL of 1 wt %  $HAuCl_4$ . The solution quickly turned a brown-red and was stirred for 30 min prior to storage at 4  $^\circ$ C (for at least 24 h before use).

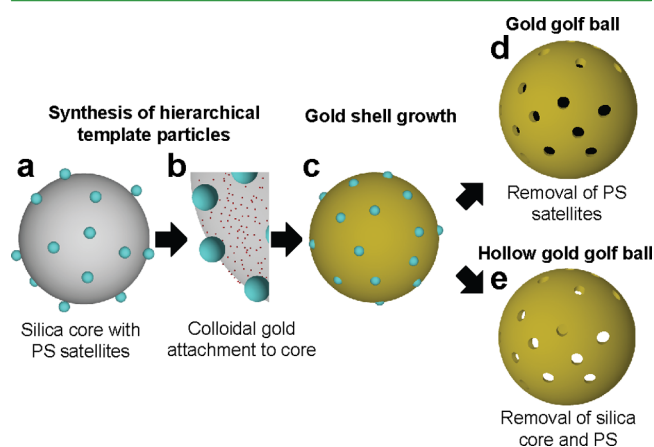
Gold seeds were attached to the hierarchical templates by adding 100  $\mu$ L of the template containing solution and 5 mL of gold seed solution together while vigorously stirring. The solution was stirred at 45  $^\circ$ C for at least 30 min. To remove excess gold seeds from the mixture, the solution was centrifuged at 1000 g for 10 min. This centrifugation step

was repeated at least 2 times. Finally, a reddish white pellet formed and was redispersed in 1 mL of water.

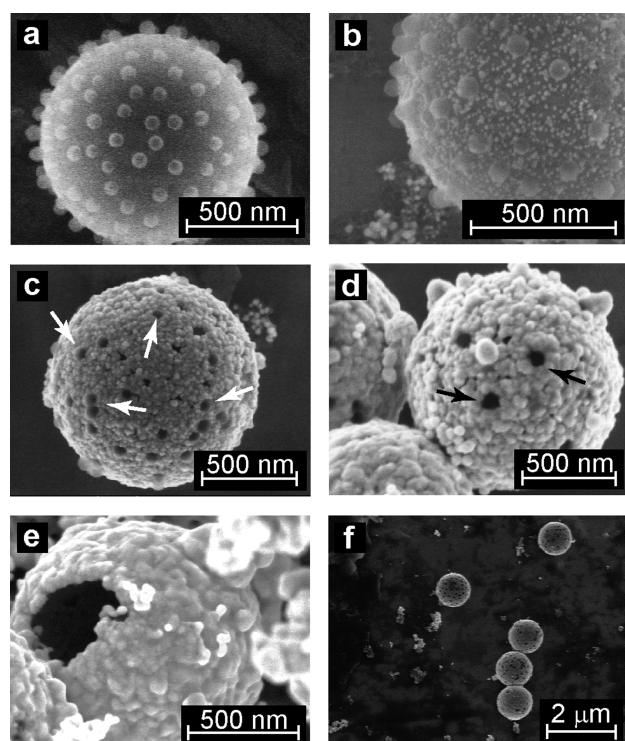
The gold seeds were grown into an interconnected gold shell through an electroless plating process as follows. A gold hydroxide ( $Au(OH)_3$ ) stock solution (183  $\mu$ M) was prepared by stirring 70 mL of 5.37 mM  $K_2CO_3$  aqueous solution for 10 min prior to the addition of 3.15 mL of 1 wt %  $HAuCl_4$ . The gold hydroxide solution was initially light yellow and became clear after 1 h of stirring prior to refrigeration. The solution was aged in dark at 4  $^\circ$ C for 24 h prior to use in plating. Then 500  $\mu$ L of gold seeded template particles were added to 15 mL of gold hydroxide stock solution and vigorously stirred for 5 min prior to the addition of 50  $\mu$ L of formaldehyde (37%). This step was quickly followed by the addition of 5  $\mu$ L of ammonium hydroxide (29%). The resulting solution was then transferred to a rotisserie and tumbled for approximately 3 h. The plated particles were centrifuged at 1000 g for 5 min, decanted to remove waste products, and redispersed in water. This step was repeated at least 4 times and finally redispersed in 2 mL of water.

Gold golf balls were created when the 100 nm polystyrene satellites were removed. This was done by solvent dissolution of the polystyrene by redispersing them in 5 mL of DMF after centrifugation. The tube containing the solution was placed in an ultrasonic water bath for 20 min at 60  $^\circ$ C followed by centrifugation at 3200 g for 10 min and redispersing in DMF. Centrifugation and rinsing with DMF was repeated twice more before redispersing in water.

Hollow gold golf balls are produced by the subsequent removal of the silica core. After removal of the polystyrene, the gold golf balls were dispersed in a 10% HF solution in 2 mL centrifuge tubes for 24 h. The golf balls were centrifuged and etched with HF once more. The hollow gold golf balls were then rinsed 6 times by centrifugation with water. Scanning electron microscopy (SEM) images for all samples were obtained using a FEI XL30 SFEU UHR SEM.



**Figure 1.** Hierarchical template scheme used in the synthesis of gold golf balls and hollow gold golf balls. (a) Silica core (gray) functionalized with a cationic polyelectrolyte (PDDA) with smaller polystyrene (PS) satellite spheres electrostatically attached. (b) Nanosized colloidal gold (red) selectively attached onto the PDDA-functionalized silica core (gold seeding). (c) Electroless plating process grows the nanosized gold seeds into an interconnected gold shell. (d) Dissolution of the polystyrene satellites completes the synthesis of the gold golf ball particles. (e) Subsequent dissolution of the silica core completes the synthesis of the hollow gold golf ball particles.

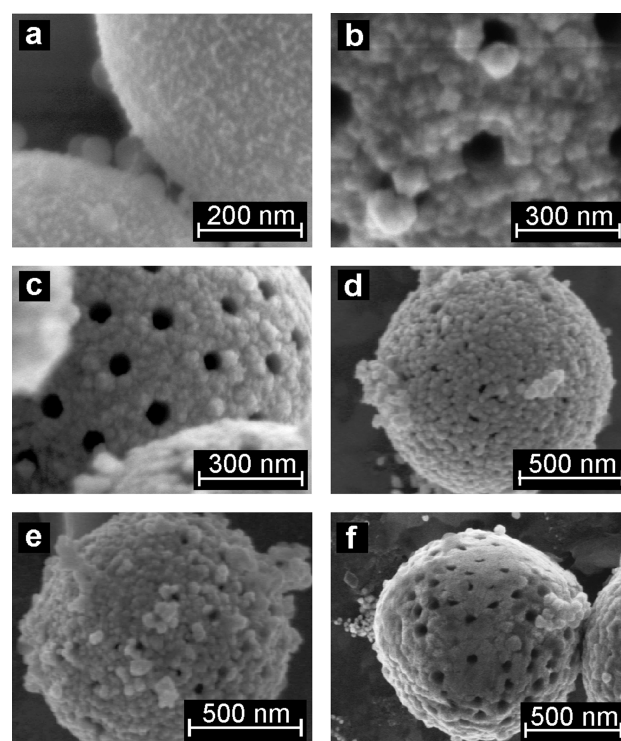


**Figure 2.** SEM images from stages of the gold golf ball synthesis process using 1000 nm cores. (a) Pollen mimicking structure formed by the hierarchical self-assembly of PDDA-functionalized 1000 nm silica and 100 nm carboxylate-modified polystyrene. (b) Nanosized colloidal gold (gold seeds) preferentially attaches to the template core. (c) After the plating process, the gold seeds can be seen as an interconnected gold shell formed around the 100 nm polystyrene satellite spheres (indicated with arrows). (d) Removal of the polystyrene leaves behind pits (arrows), resulting in the gold golf ball particle. (e) Subsequent removal of the silica core results in hollow gold golf ball particles (a broken hollow gold golf ball). (f) Wide field view of 1000 nm gold-plated template particles.

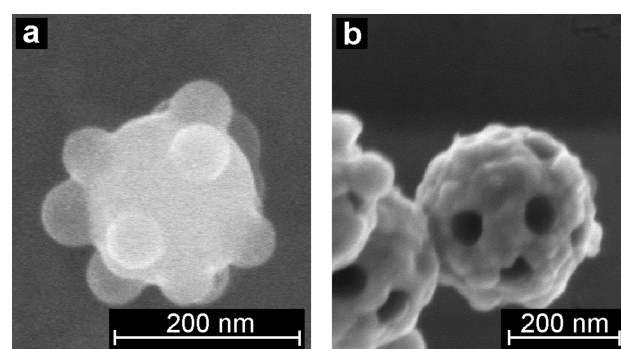
The preparation schemes of the gold golf ball and hollow gold golf ball particles are presented (Figure 1). The process consists of three major parts: (i) template synthesis, (ii) gold plating, and (iii) template dissolution. The first template was synthesized by attaching 100 nm carboxylate-modified polystyrene to a 1000 nm PDDA-functionalized silica core. By varying the concentration of the polystyrene spheres during the synthesis process, the amount of polystyrene attached to the silica core was controllable up to a limit of saturation (Figure 2a). A saturation limit was previously observed<sup>23,28</sup> and has been attributed to electrostatic repulsion limiting the number of polystyrene satellites that can attach to the surface.

Electroless gold shell growth is chemically driven by the reduction of gold ions to gold atoms. The gold atoms preferentially accumulate on preexisting gold surfaces, i.e., the gold seeds on the template cores (Figure 2b). Eventually the growing gold seeds come into contact with each other forming an interconnected gold shell over the core and around the satellites particles (Figure 2c). After the gold shell is formed, removal of the polystyrene satellites created a gold golf ball particle (Figure 2d). Subsequent removal of the silica core produced a hollow gold golf ball particle (Figure 2e). A wide-angle image of the gold golf balls is presented (Figure 2f).

The thickness and completeness of the gold shells are determined by two main factors, the surface coverage of seeds



**Figure 3.** SEM images of gold shells plated on gold seeded template particles using various concentrations of gold hydroxide or formaldehyde. Gold plated template particles using 15 mL of gold hydroxide stock solution (183  $\mu$ M) as prepared with the following amount of formaldehyde (37%): (a) 7, (b) 50, and (c) 100  $\mu$ L. Gold plating of template particles by adding 50  $\mu$ L of formaldehyde (37%) with the following amounts of gold hydroxide stock solution: (d) 2.5, (e) 5, and (f) 15 mL.



**Figure 4.** SEM images from stages of the gold golf ball synthesis process using 200 nm cores. (a) Colloidal hierarchical template particles containing PDDA-functionalized 200 nm silica cores and 100 nm carboxylate-modified polystyrene satellites. (b) After completion of the electroless gold plating process and before the removal of the polystyrene satellites.

on the template and the gold ion/template ratio. Dense gold seeding of the template cores allows gold seeds to grow into contact with neighboring seeds with minimum growth. The saturation limit for gold seeds on silica has been observed to be about 30% surface coverage in water and without salt.<sup>13,29</sup> The density of gold seeding on the template cores is expected to be near the saturation limit.

Gold shell growth on the template particles was controlled by varying two factors in our samples, formaldehyde concentration (Figure 3a–c) and gold ion concentration

(Figure 3d–f). If there are insufficient amounts of either formaldehyde or gold ions in solution the seeds will not grow to form a single interconnected shell. Insufficient shell growth results in a patchwork of large gold islands on the surface. Likewise, significant over growth of the shell will envelope the polystyrene satellites.

The limits of the size range over which colloidal hierarchical template particles can be produced has not been determined; however, the gold golf ball synthesis process was also performed using 200 nm PDDA-functionalized silica cores with 100 nm carboxylate-modified polystyrene satellites (Figure 4a). Subsequent gold seeding and plating of the smaller template particles was also successful (Figure 4b).

Using a hierarchical template constructed of two different materials, two variations of the same particle were produced with potentially very different applications. The pores of the gold golf ball have a silica bottom and may allow them to be selectively functionalized. The vacant center of the hollow gold golf ball offers storage capacity unavailable to the gold golf ball and may be used to store and release theranostic agents in the future.

Two different variants of a golf ball mimicking nanostructure were fabricated using a colloidal hierarchical template. The hierarchical template particles were fabricated by attaching smaller negatively charged colloidal polystyrene spheres (satellites) onto larger, positively charged colloidal silica spheres (cores). The PDDA-functionalized silica cores of the templates preferentially absorbed ~3 nm colloidal gold creating a dense layer of gold scattered on the surface. An electroless plating process grew the individual surface bound gold colloids into a single interconnected gold shell. Dissolution of the polystyrene satellites resulted in a gold golf ball with a silica core. Subsequent removal of the core created the hollow/porous gold golf ball. In addition, two different-sized cores were used to create templates and demonstrate the size scalability of the process. We anticipate this nanostructure may be used as a platform for site-specific functionalization or theranostic delivery.

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### Author Contributions

P.L. designed the experiments. P.L., A.G., C.D., D.C., C.E., A.P., C.Z., P.A., M.E., C.O. performed experiments. P.L., A.G., A.M. analyzed the data. P.L., A.G., A.M., and R.L. wrote the paper.

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### Notes

The authors declare no competing financial interest.

<sup>||</sup>Equal contribution.

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