

Fabrication of Hierarchical Nanostructures using Binary Colloidal Nanosphere Assembly

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Recent development in extreme ultraviolet (EUV) lithography has aided in pushing the limits of semiconductor manufacturing for next-generation consumer electronics. In addition to top-down lithography approaches, bottom-up self-assembly techniques can also provide new opportunities due to low equipment cost, especially for applications that require ordered or periodic features. One well-known technique is colloidal self-assembly using colloidal nanospheres, which results in a hexagonal closed-pack structure to minimize surface area [1]. The use of colloidal assembly with optical [2] and EUV lithography can also lead to a wide range of nanostructure geometries, which our group has previously demonstrated. However, most existing research involves the assembly of monodispersed nanospheres, which results in periodic pattern. The ability to create more complex assembly can result in smaller features and can enhance performance of photonics and nanostructured surfaces [3].

In this work we present the fabrication of hierarchical nanostructures using binary colloidal assembly. As illustrated in Figure 1, this approach is based on the group's prior work in assembly of monodispersed colloids, which has generally limited the feature size to 100 nm scale. Using a two-step coating process, we seek to create sub-50 nm features by depositing smaller nanoparticles into the voids of an array of larger polystyrene (PS) nanoparticles with hexagonal closed packed assembly. This creates a hierarchical assembly with extremely small aperture, which can be used as a physical mask for additive/subtractive micromachining or near-field lithography. Various process parameters such as the surface treatment, surface tension of solution, spin speed and concentration of nanoparticles were examined to obtain the best packing ratio. The assembly patterns were analysed using optical and scanning electron microscopy (SEM).

Preliminary results using 200 and 50 nm PS particles have been performed and the fabrication results are shown in Figure 2. Here the top-view SEM images demonstrate that the assembly pattern of the larger nanosphere forms the periodic pattern, and the smaller particles are able to fill the voids. In this process the 200 nm nanospheres are assembled using Langmuir-Blodgett assembly and the 50 nm nanoparticles were spincoated at low spin speeds. It can be observed there are voids remaining, which can be mitigated by adjusting the particle concentration in the solution. We have also developed a geometric model that can be used to predict the size of the voids in the binary assembly based on the particles diameters used. We will present the detailed fabrication process, the assembly model, and characterization of the fabricated hierarchical nanostructures. Future work aims to use the binary colloidal nanoparticle assembly mask as a near-field optical mask for lithography experiments.

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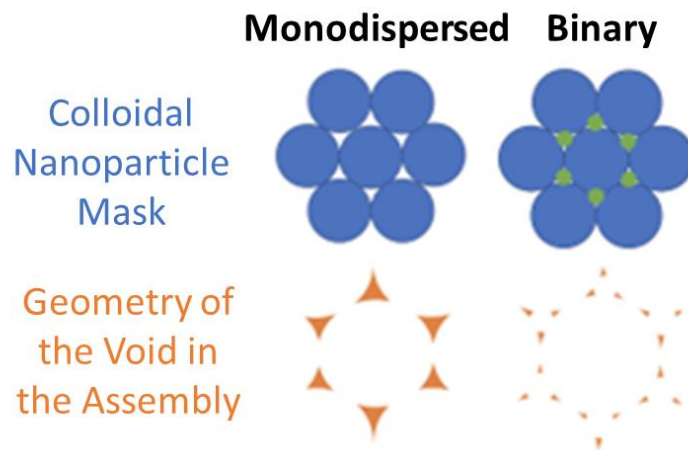


Figure 1: Comparison of a monodispersed and binary assembly for developing the geometric models. In comparing the models, the monolayer's voids are larger where the binary assembly is smaller. The model will allow the prediction of the aperture size based on the combination of the particles used.

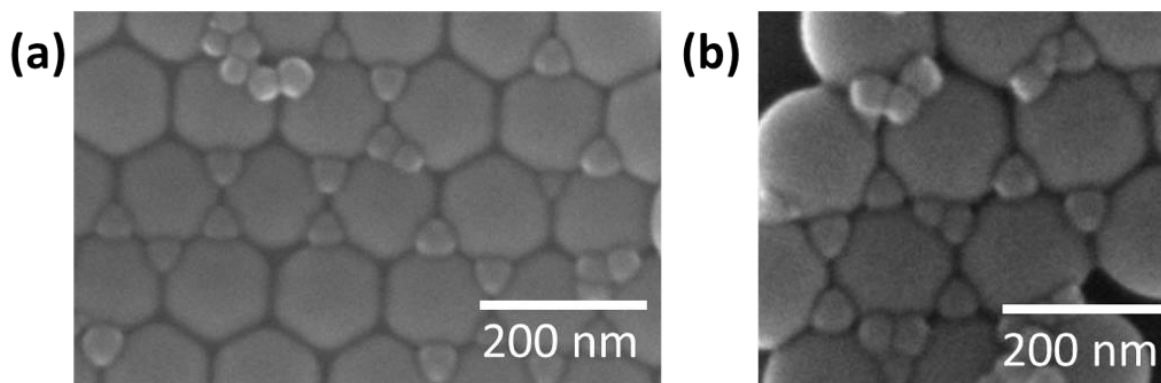


Figure 2: Initial fabrication results of the binary colloidal nanoparticles assembly. The (a) low-magnification and (b) high-magnification SEM images depicts 50 nm particles assembled in a hexagonal array of 200 nm nanospheres. These results indicate hierarchical structures can be fabricated as a mask for additive/subtractive micromachining and lithography.

¹ Hulteen, J. C.; Van Duyne, R. P. Nanosphere Lithography: A Materials General Fabrication Process for Periodic Particle Array Surfaces. *J. Vac. Sci. Technol. Vac. Surf. Films* **1995**, *13* (3), 1553–1558. <https://doi.org/10.1116/1.579726>.

² Zhang, X. A.; Chen, I.-T.; Chang, C.-H. Recent Progress in Near-Field Nanolithography Using Light Interactions with Colloidal Particles: From Nanospheres to Three-Dimensional Nanostructures. *Nanotechnology* **2019**, *30* (35), 352002. <https://doi.org/10.1088/1361-6528/ab2282>.

³ Park, K.-C.; Choi, H. J.; Chang, C.-H.; Cohen, R. E.; McKinley, G. H.; Barbastathis, G. Nanotextured Silica Surfaces with Robust Superhydrophobicity and Omnidirectional Broadband Supertransmissivity. *ACS Nano* **2012**, *6* (5), 3789–3799. <https://doi.org/10.1021/nn301112t>.