Synthesis of Shaped Nanoparticles for Two-Dimensional Assemblies

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Abstract:

Hybrid molecular orbitals with specific bonding directions provide a useful model to correlate bonding of atomic building blocks with molecular structure. The concept of directional bonding can, in principle, be translated to larger, shaped nanoparticles when these are assembled into extended arrays. Directional interactions established by chemically controlled reactive sites may promote the association of particles similar to sigma bonding of atoms in molecules. We synthesized particles that model the trigonal planar shape of sp^2 hybrid orbitals by a two-dimensional template methodology. A two-dimensional silica film was fabricated on a substrate coated with physically and chemically adhered polymer spheres. Removal of the spheres resulted in pores of uniform size and shape in the film. The optimized conditions for polymer sphere deposition to promote an ordered sphere array and creating a film on the substrate were determined. The porous silica film was removed from the substrate and separated into smaller structures through a series of etching and mechanical stress techniques.

Introduction:

Atoms are viewed as the building blocks of a molecular structure. The molecular packing geometry is dictated by the particular bonding directionality of hybrid orbitals of the atoms involved. A larger-scale model of nature's concept of directional bonding can be accomplished by shaping nanoscale particles to the same geometries as hybrid molecular orbitals and organizing these particles into ordered assemblies. The shaped nanoparticles have the unique ability to act as anisotropic building blocks for complex structures [1]. For example, directional interactions established by chemically controlled reactive sites on each particle would promote an association of particles similar to sigma bonding of atoms in molecules.

A two-dimensional template methodology was proposed for the synthesis of uniform particles shaped to model the trigonal planar shape of sp^2 hybrid orbitals. The proposed process involved: creating a polymer sphere template on a silicon wafer substrate, forming a thin film of biologically-compatible silica on the templated substrate, removing the spheres and substrate from the film, separating the film into individual nanoparticles, and functionalizing particle surfaces. This proposed triangular nanoparticle synthesis procedure was optimized.

Experimental Optimization and Results:

Prior to being used, the surface of the silicon wafer was functionalized with hydroxyl groups for favorable sphere dispersion. Spin-coating of a polystyrene (PS) sphere dispersion in a 1:1 mixture of ethanol and ethylene glycol onto a silicon wafer followed by O_2 reactive-ion etching (RIE) created a regular, non-close packed sphere array (Figure 1). To avoid aggregation and irregularity of the sphere packing, the spheres had to be well dispersed in solution prior to deposition. The O_2 etching decreased the size of each sphere, increasing the area between the spheres in the array.

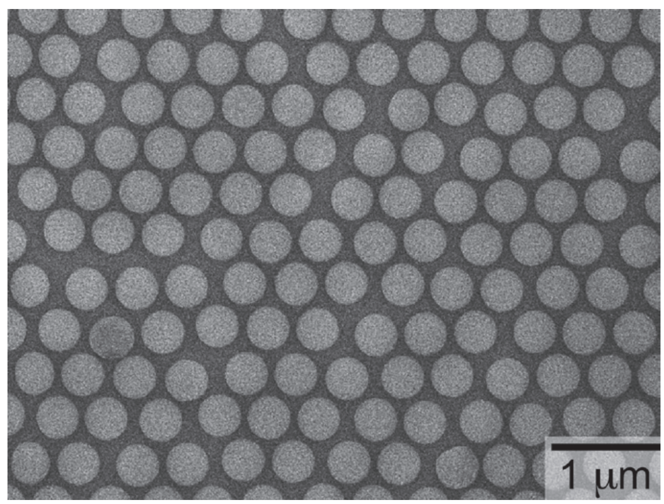

Figure 1: A top-view SEM image of ordered spheres on a substrate.

Immediately after etching, the spheres had to be further adhered on the substrate in order to keep them in place in the array. Annealing the substrate at 115ºC converted the spheres to a dome-like shape with improved adhesion. Untreated spheres were only weakly bonded to the substrate, allowing the spheres to float to the surface of the silica film resulting in a cratered-surfaced film rather than fully penetrated pores.

The strength of the sphere array before and after annealing was evaluated and diffuse UV-Vis spectral data showed significant improvement of adhesion after annealing.

The substrate surface was coated with dichloromethylvinylsilane through a chemical vapor deposition (CVD) method. Then, a silica precursor of tetraethyl orthosilicate, hydrochloric acid, and water was spin-coated onto the sphere template in a vented vessel. The surface modification was imperative for uniform film thickness and correct pore shape. Without CVD, the resulting film had curved pore walls and the film thickness was greater around the pores, but with the modification, the pores had vertical walls of consistent thickness. Adjusting the solvent evaporation rate allowed for fabrication of films with different uniform thicknesses.

Complete removal of the PS template from the film and substrate was achieved by dissolution of PS in dichloromethane and an O_2 RIE process. The nanopore film on the substrate was viewed via high-resolution scanning electron microscopy (SEM) (Figure 2). To detach the intact silica film from the silicon substrate, a combined dry etching (SF_6) and wet etching (tetramethyl ammonium hydroxide) process was developed. Figure 3 shows an SEM image of film retrieved after being removed from the substrate. The freestanding film was collected in toluene and broken up by sonication into triangular nanoparticles (Figure 4).

Conclusions and Future Possibilities:

The process for synthesizing a two-dimensionally ordered nanoporous thin film was optimized. A freestanding membrane was formed using a fast, inexpensive, and parameter-controlled approach. This structure could have future possible applications as a mask for patterned surfaces, soft-lithography, photonics, photovoltaics, separations, and bioprocess simulation.

Small-tripodal particles were produced by this optimized technique. The surfaces of these sp^2-shaped nanoparticles can be functionalized for many purposes. Most predominately, these functionalized particles could be used as building blocks for nanostructure self-assembly and other multifunctional assemblies. Other possible applications of these nanoparticles include: surface patterning, liquid crystals, and bio-targeted drug delivery. These synthetic approaches could be translated to other materials, increasing the potential uses of these anisotropic nanoparticles.

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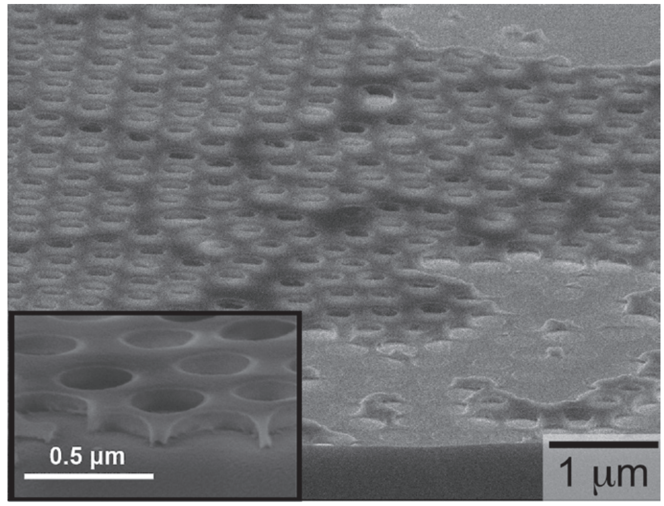
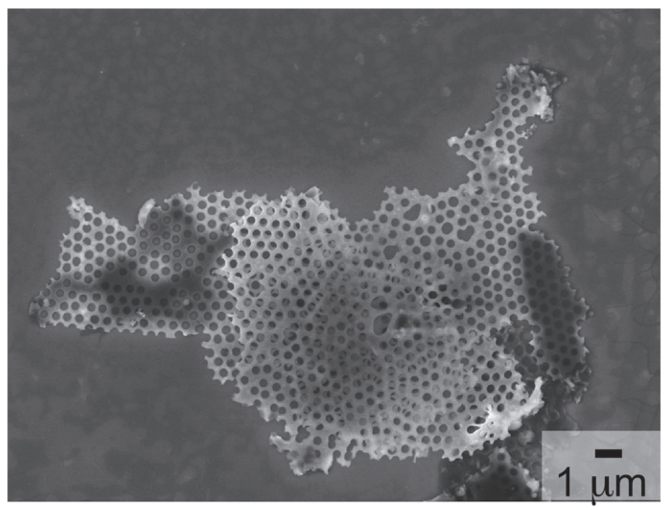
[1] Glotzer, S. C., Solomon, Michael J.; "Anisotropy of building blocks and their assembly into complex structures;" Nat. Mater, 6, 557 (2007).





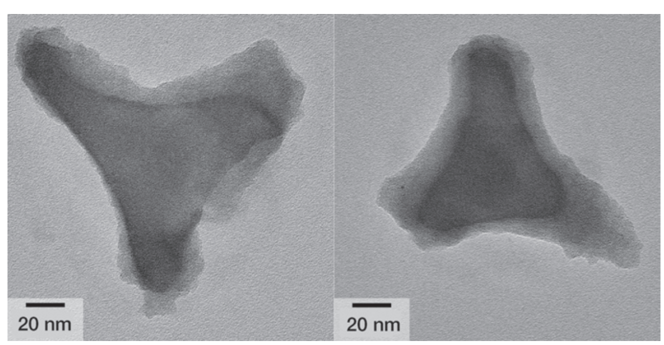


Figure 2: SEM images of porous silica films on a substrate.

Figure 3: SEM image of freestanding film collected from solution.

Figure 4: TEM images of final triangular nanoparticles.