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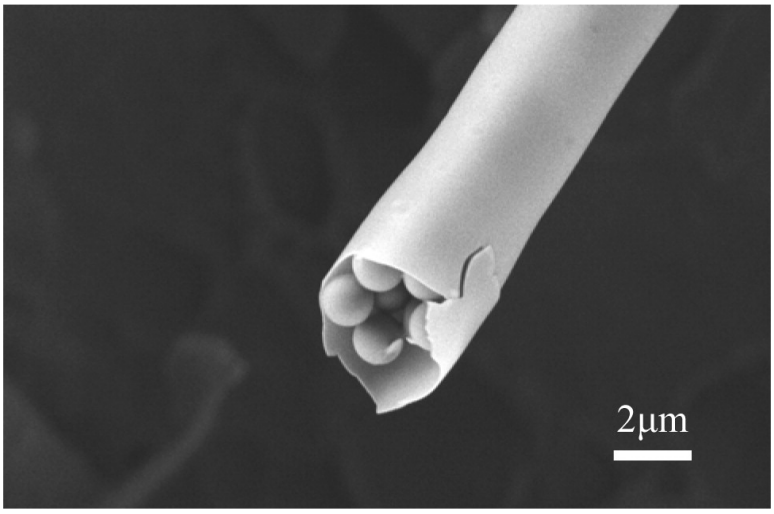

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Fabrication of Colloidal Crystals with Tubular-like Packings

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Colloidal crystals have been extensively studied over the last several years for potential applications in photonics, biomaterials, catalytic supports, and lightweight structural materials.[1] Fabrication methods based on self-assembly have predominated, resulting in large crystals and films of various thicknesses.[2] Directed assembly techniques have also been examined where colloidal spheres are constrained in cavities of set dimensions. Lithographically prepared open channels, for example, have allowed for the organization of spheres in well-defined structures; some researchers[3] have demonstrated this approach with a variety of shapes (e.g., circles, triangles, rectangles), and others[4] have prepared rigid rectangular fibers. While most of these studies have resulted in close packed arrays, some recent work has produced helical packing structures from v-shaped grooves.[5] More confined channels, such as those available in one-dimensional porous membranes, have also been examined. Moon and co-workers[6] have produced highly ordered close packed cylindrical colloidal crystals and inverse porous polymer wires, while some of us have made porous metal wires generated from mostly random packing geometries.[7] Colloidal assemblies produced within confined cylindrical channels are especially intriguing in that they can offer a variety of achiral and chiral tubular packing geometries[8,9] not expected in open grooves. Herein, we report the preparation of colloidal crystals within confined channels. Silica spheres infiltrated into 1-D channels were fused to form either colloidal−crystal wires or similar wires encased in a shear silica membrane. The packing geometries of these wires vary with the relative dimensions of the channels and result in structures not accessible by traditional assembly methods.

Colloidal crystals can be readily formed within porous silicon templates. The porous silicon is prepared by a two-step processing method primarily involving chemical and electrochemical etching.[10] SiO_2 spheres (1.3 μm) are inserted into the ca. 3 μm pores of the Si membrane by a vacuum filtration method.[7] The infiltrated membranes are then treated with a silane solution and annealed at elevated temperatures; this treatment not only serves to fuse the spheres but also encloses the spheres within silica tubes with repeated processing steps. To provide a stable support to the wires prior to removal of the silicon membrane, a metal film is deposited on one side of the membrane. The wires are then released from the template by dissolving the Si membrane in KOH solution.

Colloidal crystal wires before and after removal of the silicon membrane are shown in Figure 1a,b, respectively. The free-standing wires are typically 60 μm long and have a tendency to separate near their base. The pores in the silicon membranes used in this study are not perfectly uniform; this produces different sphere packing schemes within the colloidal wires. Typically, the spheres pack to produce wires with six helical strands, though wires can also be observed with 4−7 strands. Figure 1c−f presents representative wires having various packing schemes. Figure 1c,d shows a wire with predominately six helical strands, while the wire in Figure 1e contains four parallel strands. Intermediate to these two packing schemes, one can find chiral arrangements. Figure 1f shows a top view of four free-standing colloidal wires; the wire in the lower right contains six helical strands where the packing clearly shows a right-handed helical twist. Erickson and others have worked out the various packing schemes accessible by spheres within confined channels.[9] By controlling the channel diameter (d_c) relative to that of the sphere (d_s), it should be possible to access a wide range of tubular-like close packed chiral and achiral structures. In this study, systems where the ratio (x in $d_c = xd_s$) is in the range of 2.2−3.0 are the most prevalent. Achiral colloidal crystals with four parallel strands ($x = 2.22$, Figure 1b,e), chiral crystals with six right-handed strands ($x = 2.77$, Figure 1f), and achiral, hexagonal close packed crystals ($x = 3.0$, Figure 1c,d) are among the structures accessible by this directed assembly approach; cartoons of each of these packing schemes are shown in Figure 2a−c, respectively.

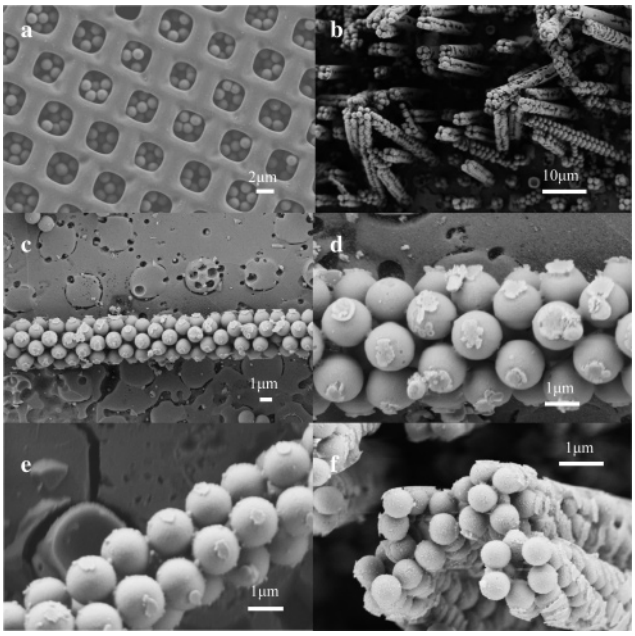

Figure 1. Scanning electron micrographs (SEM). (a) Colloidal silica spheres in a silicon membrane; (b) group of colloidal crystal wires; (c) wire showing hexagonal-like packing; (d) close up of wire in (c); (e) wire showing packing of parallel strands; (f) wires showing chiral packing (lower right).

During the annealing step, it is possible to encase the colloidal wires within a thin silica sheath (Figure 3). When the silicon membrane/silica sphere composite is repeatedly annealed and treated with silane solution, these silica tubes, ca. 20 nm thick, are observed. Figure 3 shows a series of "peapod"-like structures. As prepared, the silica sheaths are translucent (Figure 3a,b), and the silica spheres

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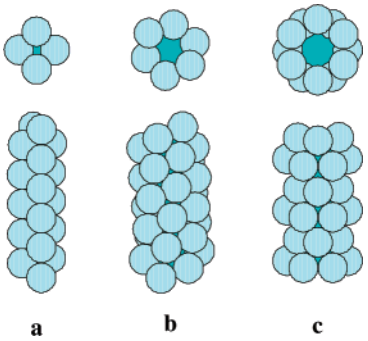

Figure 2. Top and side views of models exhibiting different tubular packing schemes. (a) Achiral packing with four parallel strands, (b) chiral crystal with six right-handed helical strands, and (c) achiral packing with six strands in a hexagonal close-packed-like structure.

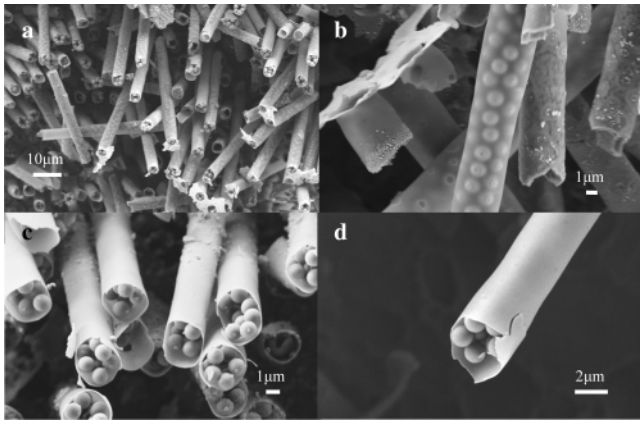

Figure 3. (a) A set of colloidal crystals within thin silica tubes; (b) close-up shows spheres within transparent tube; (c) and (d) show the ends of the tubes. Note that the samples in (c) and (d) were coated with metal to reduce charging in imaging process.

can be clearly observed within the tube. To alleviate surface charging during the imaging process, some tubes were subsequently sputtered with a layer of metal; Figure 3c,d shows the ends of several of these metal-coated silica-encased colloidal crystals where the packing at the wires' termini is highlighted. While the oxidation of the silane is thought to play some role in the formation of these silica sheaths, we suspect that the oxidation of the silicon membrane pore wall is the main contributor.[11]

The ability to control the arrangement of silica spheres in specific tubular-like packing geometries represents exciting progress in colloidal crystal formation. By simply managing the relative dimensions of the spheres and channels used in directed assembly, one should be able to access a range of chiral and achiral structures. Such assemblies are expected to offer interesting photonic properties as well as mimic a number of structures known in liquid crystals[12] and biological systems (e.g., phyllotaxis, viral capsid geometries, etc.).[9a,13] Further, while the constructs reported in this study were prepared from silica, similar preparations could be applied to a variety of other materials, for both sphere and sheath components, possibly leading to composite materials with interesting cooperative phenomena.

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Supporting Information Available: Detailed descriptions of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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