Self-Assembly of Spherical Colloids into Helical Chains with Well-Controlled Handedness

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Helical structure represents the principal element responsible for macroscopic chirality.[1] The importance of helicity can be easily appreciated from its ubiquitous presence in a variety of objects whose dimensions are scattered over a broad range of scales. Typical examples include screws and spiral springs on the macroscopic scale and α-helical motives in proteins and DNA double helices on the molecular scale.[2] Recent studies indicate that some nanostructures (e.g., carbon nanotubes[3] and thin metal nanowires[4]) may also exhibit helical morphology. The functions (and properties) of these chiral objects are largely determined by their helicity. Self-assembly provides an effective and versatile approach to the formation of helical structures although it has been limited to the molecular scale.[5] Only a few systems have been extended from molecular to nano- and mesoscales through templating or biomineralization mimicking.[6] While a number of methods have been demonstrated for assembly of mesoscale objects such as spherical colloids into long-range ordered lattices[7] and aggregates having well-defined geometric shape and structures,[8] very little progress has been made in organizing these building blocks into helical structures due to the lack of a mechanism to control the handedness. Here we combine physical confinement applied by V-grooves and capillary force to assemble mesoscale, achiral building blocks (such as spherical colloids) into helical chains. The exact handedness of these helical structures could be controlled by changing the relative orientation of capillary force with respect to the longitudinal axis of the V-grooves.

The present work was stimulated by the computational study performed by Pickett et al. in which spherical colloids were found to assemble into spiral chains when they were packed under cylindrical confinement.[9] This process was mainly driven by the excluded volume interaction (between colloids and the walls of cylindrical holes, and among colloids), a constraint that requires no overlapping between any two physical bodies. By controlling the ratio between the diameters of cylindrical holes and colloids, a number of helical structures were observed, albeit the right- and left-handed spirals appeared with roughly the same probability and the final product was a racemic mixture. Here we have changed the cylindrical holes to V-shaped grooves with triangular cross-sections (Figure 1A). Such microstructures could be routinely generated on the surfaces of Si(100) wafers through anisotropic wet etching. The edges of the triangular cross-section were approximately equal in length. As shown in Figure 1A, the physical constraint provided by the walls of these grooves can drive monodisperse spherical colloids to assemble into helical chains. The structural arrangement among these colloids is determined by the ratio between the width of the V-grooves (W) and the diameter of the spherical colloids (D). When W/D falls between 2.70 and 2.85, double-layered structures with a helical morphology will be formed (Figure 1B). The bottom layer will be an array of discrete particles that are only connected to
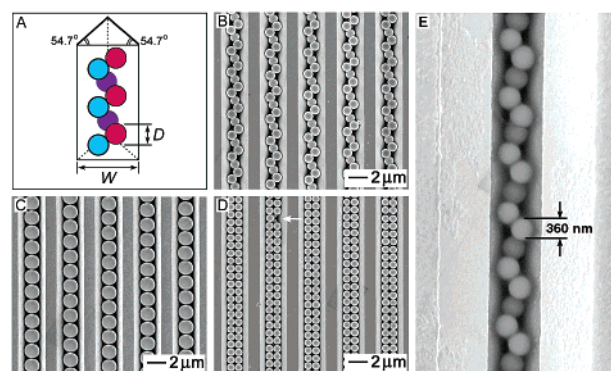
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Figure 1. Self-assembly of spherical colloids in V-shaped grooves. (A) Schematic illustration showing the formation of a helical structure. (B−D) SEM images showing three typical chainlike aggregates assembled in 2D arrays of V-grooves that had $W = 2.72 \ \mu m$. The polystyrene beads were 1.0, 1.6, and 0.8 μm in diameter, respectively. Helical structures only formed at an appropriate ratio between W and D. The arrow in (D) indicates a defect, where one can clearly see the colloids underneath the top layer of the structure. (E) A helical chain of 360-nm silica colloids that was assembled in a V-groove whose dimension had been reduced by forming hydrophobic thiolate monolayers on gold films prepared by shadow sputtering.

each other through the "dimers" sitting atop. Linear chains of colloids will be generated in the V-grooves when $W/D < 2.70$, and (100)-oriented cubic-close-packed lattices will become the dominant structures when $W/D > 2.85$. These observations agreed well with these simulation results (Figure 1, B−D). When the dimension of these V-grooves was reduced by shadow sputtering with gold (followed by formation of a hydrophobic thiolate monolayer),[11] this procedure could be extended to spherical colloids as small as ∼360 nm in diameter (Figure 1E).

A number of ways have been demonstrated to fill channels or pores with monodispersed spherical colloids such as polystyrene (PS) beads.[11] The procedure we used in this work involved the dewetting of an aqueous dispersion of PS beads from a fluidic cell that was fabricated by sandwiching a gasket (20 μm thick, cut from the Mylar film) between a glass slide (on the top) and a Si(100) wafer.[12] The surface of this Si(100) substrate had been patterned with an array of V-grooves using the combination of photolithography and anisotropic wet etching.[13] As the liquid slug dewetted from the fluidic cell, a meniscus was formed at its rear edge (see Figure 2A). The capillary force (F_c) originated from this meniscus was strong enough to push all PS beads into the V-grooves and left almost no beads on the top surface of the Si(100) wafer. Figure 1B shows scanning electron microscopy (SEM) image of spirals that had been assembled into an array of V-grooves using this method. In this case, $W = 2.72 \ \mu m$, $D = 1.00 \ \mu m$, and $W/D = 2.72$. The "dimers" were titled by ∼46° against the longitudinal
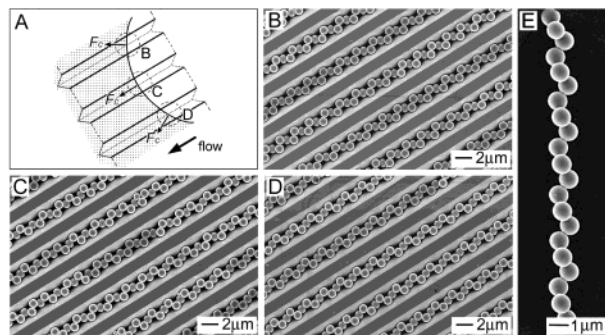
Figure 2. (A−D) SEM images of helical chains with different chiralities that were obtained with the capillary forces oriented toward different directions relative to the longitudinal axis of the V-grooves. The schematic in A shows the relative locations where the structures in B−D were obtained. It was possible to dice the Si(100) substrate into three pieces along the longitudinal direction of V-grooves, with each piece corresponding to a specific region shown in A. As a result, one could separate each sample into optically pure isomers. (E) The SEM image of a free-standing helical aggregate after it had been welded by thermal annealing and subsequently released from the original template.

axis of the V-grooves. When substrates diced from the same Si(100) wafer were used and the diameter of PS beads was changed to 1.6 and 0.8 μm, linear chains (Figure 1C) and cubic-close-packed lattices (Figure 1D) were obtained as the final structures, respectively. These two chainlike structures were obviously achiral. In the latter structure, the "dimers" were oriented perpendicular to the longitudinal axis of the V-grooves. These results demonstrated that it was possible to assemble spherical colloids into multiple copies of helical chains by judicially choosing appropriate building blocks to match the dimensions of V-grooves.

It is also interesting to note that all spiral chains shown in Figure 1B had the same sense of rotation (in this particular sample, right-handed). We did some additional work to study the mechanism responsible for the breaking of symmetry and thus the formation of pure enantiomers. It was found that the exact handedness of these spiral chains was determined by the direction of capillary forces relative to the longitudinal axis of V-grooves. When a slug of colloidal dispersion flows through the thin fluidic cell, the rear edge of this slug becomes highly curved due to the formation of a meniscus (Figure 2A). This spontaneous curving process divided the surface of silicon substrate into three regions (B−D, as labeled in Figure 2A). The corresponding structures observed in different regions are shown in Figure 2, B−D. Obviously, regions (B) and (D) were left−right mirror images, and helical chains obtained from these two regions exhibited opposite signs of rotation. The spiral chains in each region were homochiral and could easily expand to lengths >100 repeating units without changing their handedness. The exact rotation of these spiral chains depended on how the liquid front was curved relative to the flow direction. When the rear edge of liquid slug curved toward the right side (as viewed along the direction of liquid flow, region B), the capillary force (F_c) drove the spherical colloids into left-handed spirals, and bending to the left side (region D) led to the formation of the other pure enantiomer. In region (C) where the capillary force was parallel to the longitudinal axis of V-grooves, both left- and right-handed helical senses were equally probable, and intrachain helical reversal might also occur. As illustrated in Figure 2C, the handedness of each segment within an individual spiral chain were randomized.

Once formed, the helical structure could be preserved by welding together the building blocks within each spiral chain into a single piece. Adhesion between adjacent polymer beads could be introduced by annealing the as-prepared sample at a temperature slightly

higher than the glass-transition temperature of the polymer.[14] The surfaces of adjacent building blocks could be permanently fused as a result of the thermally induced viscoelastic deformation. The final structures could then be released from their templates using sonication. Before the template was used in the self-assembly process, its surface could also be sputtered with a thin layer of Au or Al to facilitate the lift-off process. Figure 2E shows the SEM image of a free-standing, helical chain of PS beads that was released from its original V-groove after it had been annealed at 96 °C for ∼10 min. Note that each PS bead is connected with two adjacent colloids to form a robust, chiral structure.

In summary, we have demonstrated that physical constraint and capillary force could be combined to provide a generic approach for the self-assembly of achiral building blocks (e.g., spherical colloids) into helical mesostructures having well-controlled handedness. The ability to process an achiral material into helical structures having well-controlled handedness should allow us to obtain new functionalities (e.g., optical activity) that this material otherwise does not exhibit.[15] The self-assembly process described here may also shed light on the mechanism(s) by which pure enantiomers with a particular handedness evolved in nature.[16]

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