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Inorganic Double Helices

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Inorganic Materials with Double-Helix Structures[**]

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The helix is a fantastic form in nature, science, art, and architecture, a space curve form with a constant slope. One representative work of art is the famous sculpture *The Rape of the Sabine Women* by Giambologna (1529–1608) in Florence; a counterpart in architecture could be the staircase of the Vatican Museum (Figure 1). The most important (double) helix structure in nature is deoxyribonucleic acid (DNA, Figure 2a). A DNA helical chain consists of two polynucleotide strands running "antiparallel" with a specific interaction through hydrogen bonding. Other biological polymers such as collagen and agar produce helical chains from the nanometer to the sub-micrometer scale. α-Amylose is a macromolecule with a helical structure that contains about six glucose units per helical turn. Peptides can adopt an α-helical structure or form larger helical arrays as found, for example, in the collagen triple helices.

The fascinating morphology of the helix has stimulated many synthetic efforts to mimic its unique form. In chemistry, especially in organic chemistry,[1] artificial helical supramolecules can be designed by conformational restriction of macromolecules,[2] inter- or intramolecular hydrogen bonds,[3,4] or coordination to metal ions.[5–7] Metal complexes that contain one or more ligand strand and two or more metal centers are called "helicates".[8] Helical polyacetylene can be generated through asymmetric polymerization in a chiral liquid-crystal field consisting of a chiral nematic liquid crystal, even though an acetylene monomer has no chiral moiety.[9] Through noncovalent bonding interactions with a specific chiral guest, synthetic polymers fold into a single or double helix with preferred handedness.[10] Figure 2b shows a double-helical oligomer that consists of two complementary molecular strands bound together through amidinium–carboxylate salt bridges. It remains a tremendous challenge to understand the fundamental principles of molecular recognition and (self-) assembly of the new supramolecular functional devices, their construction, and their application.

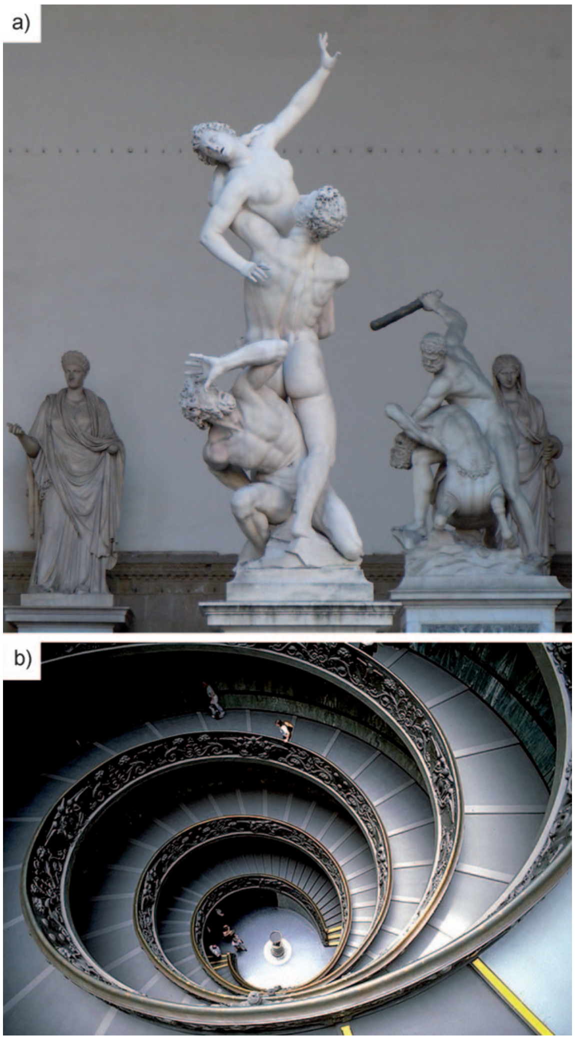

Figure 1. a) The Rape of the Sabine Women (1574–82), Giambologna, Florence. b) The staircase of the Vatican Museum (from http://en.wikipedia.org/wiki/File:VaticanMuseumStaircase.jpg).

In materials science, it was reported as early as 1929 that several organic and inorganic crystal systems induce twisted shapes.[11] In contrast to supramolecules or polymers with helical structures, macroscopic helical morphologies of inorganic materials are formed without microscopic chirality,

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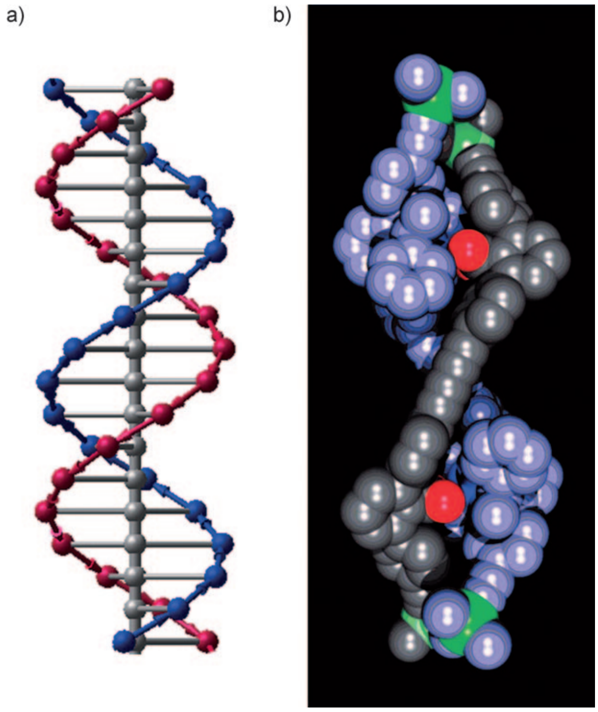

Figure 2. a) Structural model of the DNA double helix; b) structure of a double-strand helical oligomer; gray/blue: C skeletons of both strands, red: O in amidinium carboxylate salt bridges, green: Si in trimethylsilyl groups. From Ref. [10].

and thus there is no molecular recognition or (self-) assembly involved in the formation of inorganic helical structures. The template method has been successfully used to transcribe the helical structure of organogel fibers onto inorganic materials. For instance, right- and left-handed helical silica structures can be created by transcription of right- and left-handed structures, respectively, in diaminocyclohexane-based organogel fibers.[12]

Besides the templating method, some specific crystallization processes can also produce inorganic materials with helical morphology. It is reported that helical morphologies can grow with triclinic crystals in various kinds of gel matrices.[13] The backbones comprise twin crystals twisted with a constant angle. The emergence of the macroscopic chiral morphology from achiral components can be attributed to twisted assembly of tilted subunits. A structural model of such twisted assembly of tiled units is shown in Figure 3. The formation of helical structures is ascribed to the change of growth behavior from a kinetic-limited mode to a diffusion-limited mode with suppression of the mobility of the solutes in the presence of gelling agents.[14]

Helical morphologies were generated from aspartic acid crystals in agar gel matrix.[15] Helical whiskers can be produced by vapor-phase deposition techniques; the structure originates from the asymmetric behavior of a growth site at the top of each whisker[16,17] and from dislocations in the crystal phase.[18] It is also reported that the formation of helices of achiral $BaCO_3$ nanocrystals can be induced by racemic block copolymers through tectonic arrangement of these nanocrystals.[19] $BaCO_3$ nanofibers with double-stranded and cylindrical helical morphologies were generated by mineralization controlled by a phosphonated block copolymer.[20]

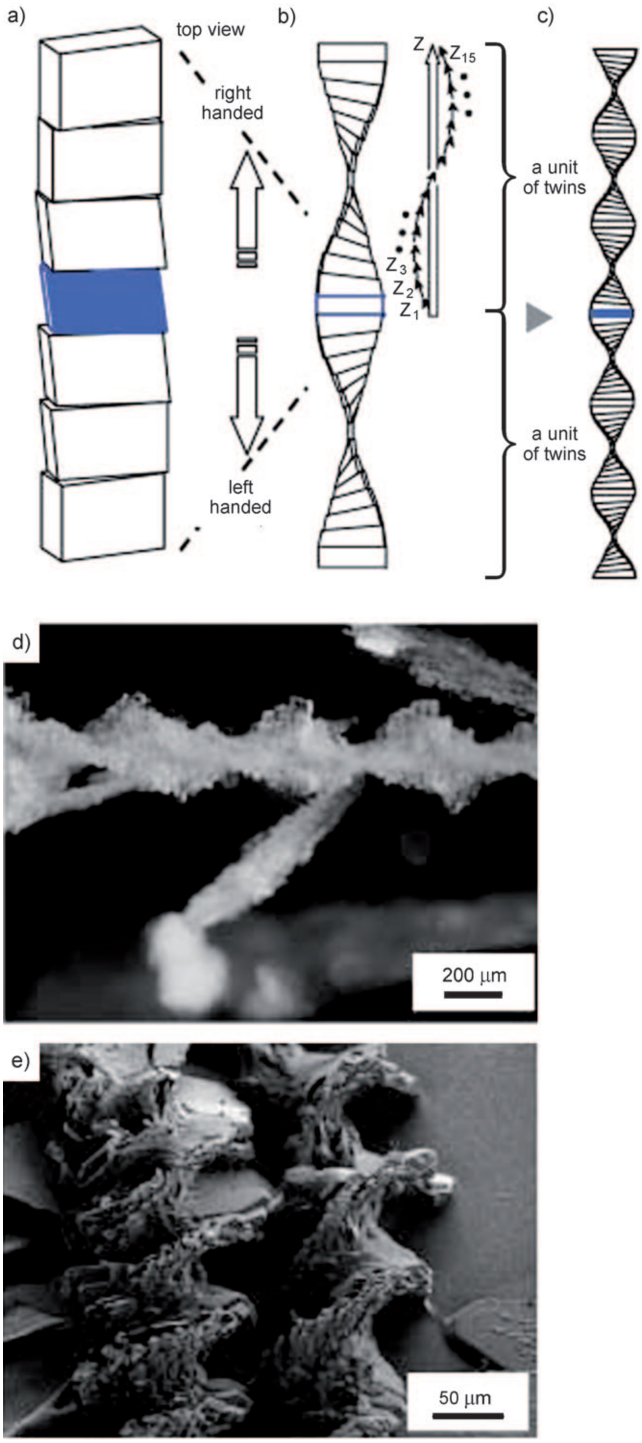

Figure 3. A three-dimensional growth model and formation mechanism of helical morphology in a diffusion field. a) The upward and downward accumulation of subunits induces the right- and left-handed twists, respectively. b) Right- and left-handed units of twins are produced from the nucleation point. The growth direction (Z_1–Z_{15}) is finally adjusted to Z. c) A pile of units forms helices; the specified direction of twist does not change during growth. d, e) Twisted and helical morphology of triclinic crystals. Reprinted with permission from Ref. [13].

While some advances have been achieved for inorganic materials with a single-helical conformation, reports of counterparts with double-helix structure are rare. Recently, double-helical silicon microtubes and double-helical carbon nanotube (CNT) arrays were prepared by two quite different methods.[21,22] Marito and Yamane used a common phenomenon in which a liquid (here a melt of NaSi) with a high inner pressure will, when passing through a hole or a vent, form jet-like tubes; this property is used to prepare nanostructured silicon.[21] For their experiment, they used a disk of powdered NaSi loosely compacted in an Ar-filled glove box. Argon gas fills the spaces between the grains in the compacted disk (Figure 4a). When the disk is heated to high temperature, silicon crystallizes to grains and sodium evaporates from the surface and inside of the disk through the spaces. At around a eutectic temperature of 750 °C, the disk remains a solid, but some pockets of NaSi melt with Ar gas are trapped in it (Figure 4b). The melt pockets together with Ar move toward the disk surface by dissolving Si at the grain boundary near the surface and recrystallizing Si inside the disk (Figure 4c). Once the melt is exposed on the disk and the gas pressure in the melt of a protuberance is high enough, the melt is pushed out and elongated to form a tube (Figure 4d). The volume of the tube is rapidly decreased by evaporation of Na and crystallization of Si to form nanotwins (Figure 4d,e). The silicon the authors obtain is not tubular but has a double-helical structure. The volume decrease is believed to be the driving force for the formation of the double-helical structure (Figure 4 f). It is apparent that the formation of the double-helical microtubes is realized by a very delicate balance between the inner pressure of the melt in the protuberance and the viscosity of the melt. If the viscosity is too high, the protuberance cannot be elongated, and if it is too low, the gas is easily released from the top of the protuberance.[21] The formation of the melt containing Ar gas inside the disk is necessary for the formation of the protuberances and Si microtubes. But how the double-helical morphology is finally formed and whether their growth follows the mechanism explained in Figure 4 remains a puzzle. Further experiments are needed to verify the hypothetical mechanism and to find a way to control the length and diameter of the tube.

In the same issue of *Angewandte Chemie International Edition*, arrays of carbon nanotubes (CNTs) were reported to be found among the products of a chemical vapor deposition (CVD) process.[22] In contrast to many other CVD processes, which are the standard technique for production of CNTs, layered double hydroxide (LDH) flakes with active catalyst nanoparticles on both sides were used for the catalytic growth of CNTs. LDHs are a class of synthetic two-dimensional (2D) nanostructured anionic clays and served as 2D lamellar substrates. When a carbon source was introduced into a CVD system containing Fe-loaded LDHs at high temperature, aligned CNTs grew on both sides of the flake. This behavior is expected and is a very common process for CNT production. But how is a double-helical CNT array formed during this CVD process? Zhang et al. believed that the double-helical morphology is formed when the CNT tips meet space resistance at the very beginning of growth.[22] Thus the CNT strands can grow only in a twisted manner. A double helix is then formed with CNT arrays from each side of a LDH flake as the "backbone". The proposed mechanism is illustrated in Figure 5 together with an SEM image of an obtained CNT-array double helix. The prerequisite of this formation hypothesis is that the CNT arrays on both sides of the LDH

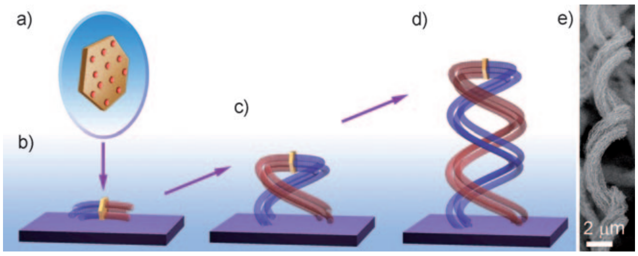

Figure 5. a–d) Illustration of the formation of the CNT-array double helix. An Fe(Co)/Mg/Al LDH flake was used as the substrate. e) SEM image of the obtained CNT-array double helix. Reprinted with permission from Ref. [22].

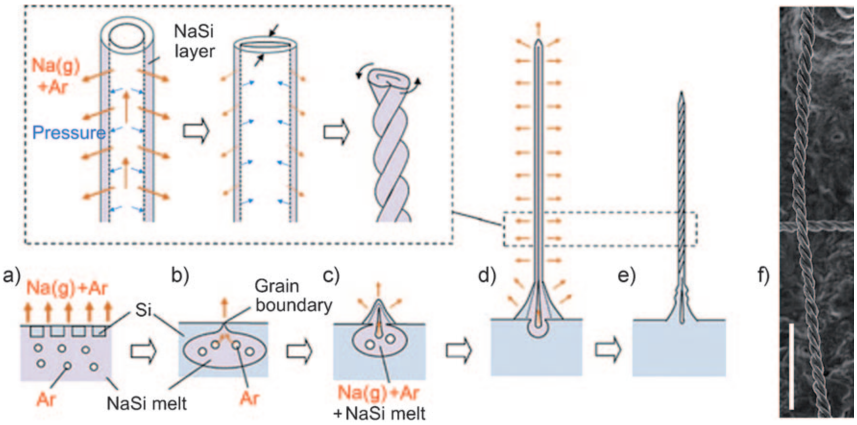

Figure 4. Proposed formation mechanism of double-helical Si microtubes. a) The disk surface is densely covered with Si grains (Na(g) = gas-phase sodium). b) Some pockets of NaSi melt with Ar gas are trapped in the disk. c) The melt is exposed on the disk surface to the gas phase through the vent at the grain boundary, and protuberances are formed on the surface. d) The melt is pushed out and elongated to form a tube. e) The double-helical structure is formed by the evaporation of Na. f) SEM image of a double-helical Si microtube. Scale bar: 100 µm. Reprinted with permission from Ref. [21].

flake do not grow straight but curve as shown in Figure 5c. The real reason for this unusual growth behavior is not clear. Here also, further experiments are needed to verify the proposed hypothetical mechanism.

The two reports highlighted herein show that inorganic materials with macroscopic double-helical morphology can be prepared. Although the methods used and the mechanisms proposed in these two studies are completely different and not related to each other, they generate nano- and microsized materials with double helices. Furthermore, both methods are template-free. There is no microscopic chirality at the atomic scale. Silicon with its cubic structure (space group $Fd\bar{3}m$) cannot form macroscopic double-helical morphologies without introducing defects, especially planar defects or twinning, into its structure. Microtwinning and nanotwinning were found as the main structural motifs of double-helical Si microtubes.[21] A structural model at the atomic level is needed to explain the Si tubular double helices.

As for the CNT-array double helices, the majority of CNTs in the double helix are double-walled ($>95\,\%$) with an inner diameter of 4–6 nm.[22] CNTs in the double helix must contain more defects than CNTs with straight morphology, which possibly results from the regular insertion of pentagon–heptagon pairs. It should be mentioned here that only CNT-array double helices have been obtained. It remains a challenge to synthesize a true CNT double helix in which each backbone is one single-walled CNT with its own chirality.

The common features among various helical structures, regardless if they are biological or inorganic, include structural stability and artistic beauty. The sculpture of Giambologna (Figure 1a) is an aesthetic masterpiece. He solved the complex spatial problems of three intertwined figures in the unique spiral-like form. The statue renders a dynamic panoply of emotions in poses that offer multiple viewpoints. The staircase of the Vatican Museum (Figure 1b) is an optimal combination of architecture and art: it has the common function of stairs, which is, however, harmonically realized in a spiral form with its intrinsic beauty. The double-helical structure of DNA is a stable structure imprinted with highly ordered genetic codes, capable of precisely replicating itself and transmitting genetic information from one generation to the next, thus highlighting the ultimate beauty of living organisms.

Evolutionary pressure makes nature quite economical with inventions, and thus the final question remains: Is our intuitive understanding of beauty deeply linked to usefulness? If so, we might surmise that the newly reported double-helical inorganic materials are not simply elegant but may have practical applications. Inorganic materials with double helices could be interesting for morphology-related applications, for instance, in micromechanics or nanoelectrodynamics. We know that when a current is applied to a coil of conductive materials a magnetic field will be induced. The new structures might serve as a starting point for the study of electromagnetic phenomena at the nanoscale. If we have double-helix devices consisting of two coils, and parallel or inverse current can be applied to each "backbone", we may study materials or physical properties of the double helix. There are no reports on such fundamental studies. But the ability to prepare inorganic materials with such morphology, as reported in the two highlighted papers, opens the possibility for such studies. We see the light on the horizon that inorganic double-helical materials can be obtained without template methods; the challenge, however, remains for materials scientists and chemists to develop synthetic tools and receptors to produce such materials by design rather than to find them by chance in the product. When this goal is realized, we will have a new era of systems chemistry and thus the true possibility to explore the application of inorganic materials with double-helical morphology in chemistry and biology. The recent development in electron microscopy using vortex electron beams with spiraling wavefronts[23] provides a timely tool for the investigation of physical properties and for the manipulation of such nanomaterials with double-helical structures.

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