

# Metal-Driven Hierarchical Self-Assembled One-Dimensional Nanohelices

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## ABSTRACT

Sophisticated helical structure has been an attractive subject due to its significance in understanding of biological self-assembly and appealing application in nanoscience. In this work, a facile route toward one-dimensional helical nanostructure is presented based on metal-cholate supramolecular self-assembly. Well-defined right-handed helical nanoribbons in calcium-cholate systems are systematically investigated and a series of metal ions are exploited to drive metal-cholate supramolecular helix. It is anticipated that the incorporation of metal ions may endow versatile functionalities and merits to the self-assembled nanohelices. Particularly helical inorganic nanomaterials (i.e., SiO<sub>2</sub> and ZnS) have been prepared based on metal-cholate supramolecular nanohelix via two distinct templating strategies.

Helix is a central structural motif for biological systems, ranging from nanoscopic DNA double helix and collagen triple helix to microscopic viruses and macroscopic sea shells. Inspired by the elegance and complexity of natural helical assemblies, chemists have endeavored in creation of well-defined, functional helical structures via molecular self-assembly route.<sup>1</sup> Molecular self-assembly based on rational control of noncovalent interactions such as hydrogen bonding, aromatic stacking and/or metal coordination interactions etc., provides powerful tools for the design of hierarchical structures of nano- to micrometer scale.<sup>2</sup> Nevertheless, it remains a fundamental challenge to fabricate helical assemblies from artificial molecules considering complicated organic synthesis, such as oligo(p-phenylenevinylene)s,<sup>3</sup> oligo(p-phenyleneethynylene)s,<sup>4</sup> sugar-lipid,<sup>5</sup> hexabenzocoronene amphiphiles,<sup>6</sup> and novel polymers.<sup>7</sup> Alternatively, several groups have taken advantage of natural biomolecules including model bile,<sup>8</sup> lipid,<sup>9</sup> and polypeptide,<sup>10</sup> which are the survivals of natural selection, to mimic the helical structures. However, these helical structures are always achieved with complicated preparing process and/or high

cost. The knowledge of helical architectures will not only lead to a better understanding of nature and life, but will also enable a variety of applications in material science, chiral catalyst, nonlinear optics, asymmetric synthesis, sensing, chiral devices, and so forth.<sup>11</sup>

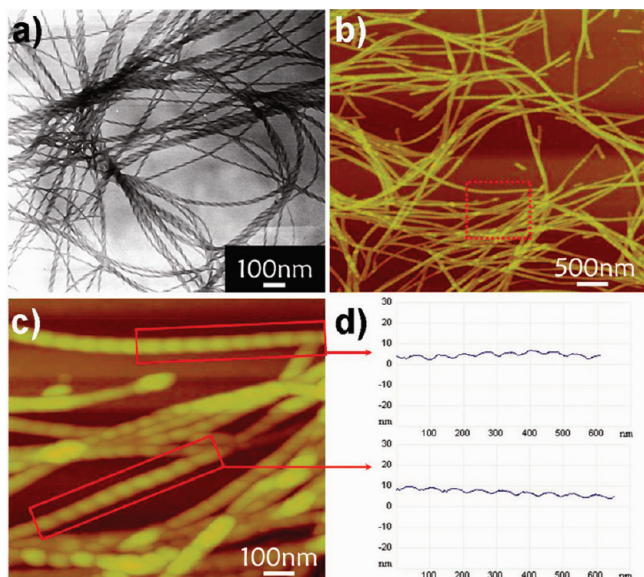
Herein, we provide a facile route to fabricate aesthetic self-assembled nanohelix based on metal-cholate supramolecular system (MCSS). By directly mixing the stock solution of sodium cholate (SC) and metal ions, self-organized hierarchical nanohelix can be conveniently obtained. SC is a biocompatible, nontoxic, and biodegradable biosurfactant, which can be applied in biology-related field. Metal ions, which are versatile in diverse subject areas,<sup>12</sup> are introduced to drive the supramolecular self-assembly of SC. It is therefore anticipated that the incorporation of metal centers may endow versatile functionalities and merits to self-assembled nanohelices. Particularly in the field of material science, metal-cholate supramolecular nanohelices can be used to direct helical inorganic materials. In preliminary attempts, helical silica and ZnS nanomaterials have been prepared via traditional sol-gel process and self-templating approach.

In this report, calcium-cholate supramolecular system with 20 mM calcium nitrate and 20 mM SC was systematically investigated. Transmission electron microscopy (TEM) was used to visualize the self-assembled nanostructures. Figure 1a demonstrates the formation of 1 D helical structure with

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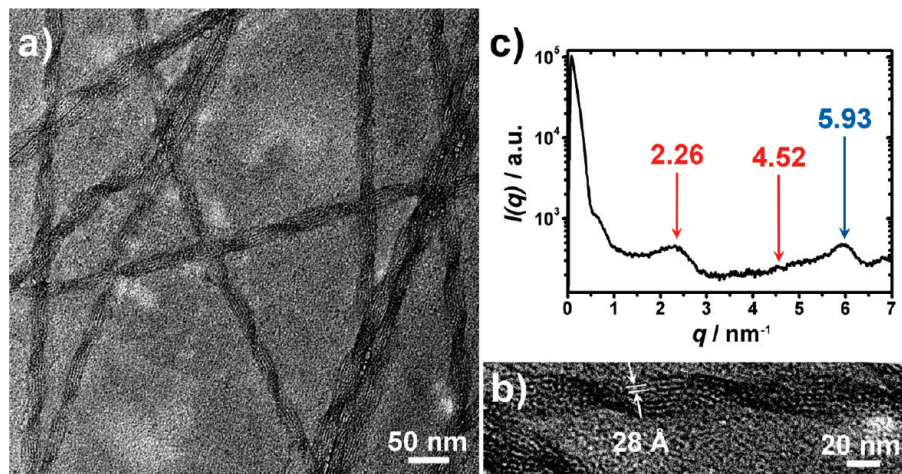
**Figure 1.** Morphology of calcium-cholate supramolecular nanohelices. (a) Typical unstained TEM image of right-handed nanohelices; (b) tapping-mode AFM height image revealing the helical undulate feature; (c) high-magnification of the boxed area in (b); and (d) corresponding cross-sectional analysis of nanohelices showing the uniform pitches.

micrometers' length. The helices exhibit flexible twisted shape of the nanoribbons with uniform right-handed bias with about 70 nm helical pitches, several nanometers thickness and 10–40 nm width. Surprisingly, the well-defined right-handed helical structure is the exclusive morphology under the scope of TEM. The height images obtained by tapping-mode atomic force microscopy (AFM) on clean silica sheet confirm the helical undulate feature and high-axial-ratio structures (Figure 1b,c). Sectional analyses of Figure 1d reveal uniform nanohelices with a height of 5–10 nm and pitches of  $71 \pm 2$  nm, which are comparable to the results of TEM. However, compared to the TEM image, the nanohelices under AFM have a relatively wider diameter of about 60 nm. This may originate from AFM tip broadening

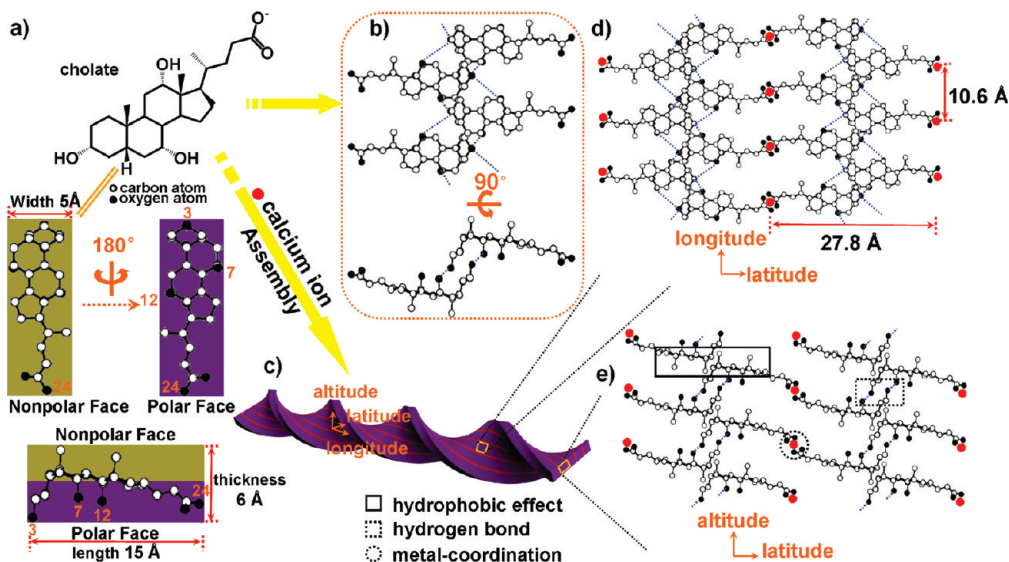
effect, which arises when the radius of curvature of the tip is comparable with, or greater than, the size of the object to be imaged.<sup>13</sup>

To reveal the superstructure of nanohelices, high-resolution TEM (HR-TEM) and small-angle X-ray scattering (SAXS) were further employed. In HR-TEM image (Figure 2a), the longitudinal darker lines along the nanoribbons that twist into helices strongly manifest the helices are constructed by uniformly parallel, longitudinal, and alternatively distributed stripes across their entire width. The stripes with a deeper color than carbonic skeleton may illuminate the position of metal ions. Enlarging a segment in Figure 2b shows the stripes are at a periodicity of 28 Å, which is close to twice as long as cholate backbones length ( $15 \text{ \AA} \times 2$ ). SAXS from metal center, which couples to cholate carboxyl group, permits a complementary picture of nanohelix in situ (Figure 2c). A strong scattering signal ( $q = 2.26 \text{ nm}^{-1}$ ) along with higher-order reflection peaks ( $q = 4.52 \text{ nm}^{-1}$ ) could be found, which corresponds to a  $d$ -spacing of 27.8 Å and agrees well with the period of strips in HR-TEM. Another prominent reflection signal is observed in the high  $q$  region at  $5.93 \text{ nm}^{-1}$  ( $d = 10.6 \text{ \AA}$ ). This distance is comparable with twice the width of cholate skeleton ( $5 \text{ \AA} \times 2$ ).

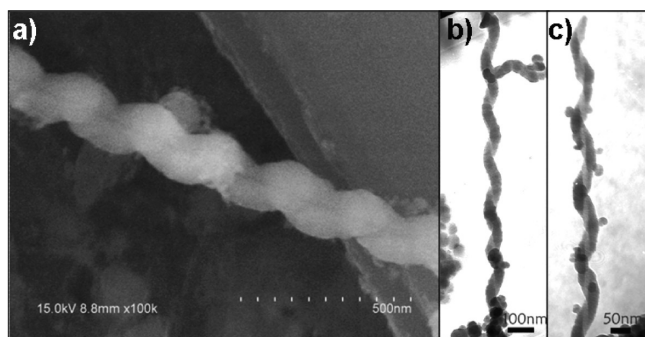
Combined with SAXS and HR-TEM, a possible scheme of molecular packing in nanohelix was proposed. SC is a well-known facial amphiphile that composed of a rigid steroid skeleton with a polar face and a nonpolar face (Figure 3a). Three hydroxyl groups and a carboxyl group were directed to polar face, and two methyl groups to the nonpolar face. Owing to the hydrogen bond between hydroxyl groups, cholate can assemble into a unique bilayer structure,<sup>14</sup> in which hydroxyl group at the C3 position in one molecule links two hydroxyl groups at C7 and C12 in the other two molecules related by a 2-fold screw axis (Figure 3b). Upon addition of calcium ions, cholates self-assemble into well-defined helical nanoribbons as described in Figure 3c. The red lines in Figure 3c, corresponding to the darker stripes in HR-TEM, are deemed as calcium ions. In the longitude dimension, cholates adapt bilayer strip structure via H-bond



**Figure 2.** Superstructures of  $\text{Ca}^{2+}$ -cholate supramolecular nanohelices. (a) Unstained HR-TEM image of the nanohelices showing the twisted nanoribbons are composed of uniformly parallel, longitudinal stripes across their entire width; (b) enlargement of HR-TEM image of a segment of the coassembly demonstrates the periodicity of stripes is 28 Å; and (c) in situ SAXS profile.



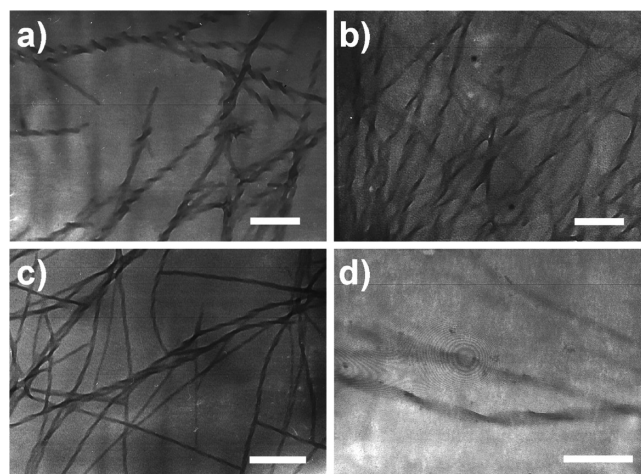
**Figure 3.** Schematic model of the helical nanoribbon. (a) Molecular structure and backbone of cholate illustrating the facial amphiphilicity and molecular size; (b) the molecular aggregate that is the minimum constitution unit of a bilayer type of cholate host framework (the blue dotted lines denoted H-bond); (c) scheme of twisted nanoribbon composed of parallel, longitudinal stripes; and (d) top view and (e) cross-section view of the helical model.



**Figure 4.** (a) SEM and (b,c) TEM images of helical SiO<sub>2</sub> by sol-gel transcription.

(Figure 3b,d). In latitudinal dimension, these bilayer strips approach together via calcium-carboxyl coordination. The existence of calcium-carboxyl coordination is evidenced from Fourier transform infrared (FT-IR), (Supporting Information, Figure S1 and S2) and electrospray ionization mass spectra (ESI-MS) (Supporting Information, Figure S3). According to SAXS, the periodic distance in the latitudinal and longitude dimension is 27.8 and 10.6 Å. In altitudinal dimension, two cholate bilayers adapt a nonpolar face-to-nonpolar face arrangement driven by hydrophobic effect (Figure 3e). It is hence proposed that metal-cholate supramolecular nanohelix is constructed by the synergic effect of multiple noncovalent interactions, such as hydrogen bond, calcium-carboxyl coordination and hydrophobic effect.

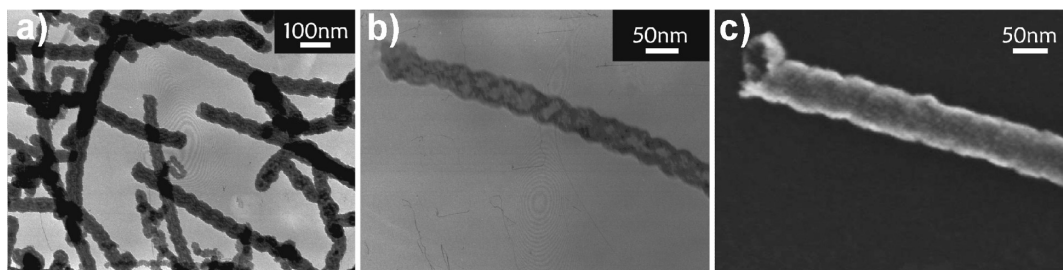
The elegant soft nanohelices built by calcium-cholate supramolecular self-assembly can be further transcribed into helical silica materials via traditional sol-gel process.<sup>15</sup> In this strategy, tetraethyl orthosilicate (TEOS) is introduced into calcium-cholate supramolecular system followed by the addition of ammonia as catalyst. The hydrolysis products of TEOS are supposed to assemble around supramolecular nanohelices through H-bonding. Subsequently after poly-



**Figure 5.** TEM images of self-assembled nanohelices by SC solution in the presence of (a) Ni<sup>2+</sup>, (b) Zn<sup>2+</sup>, (c) Co<sup>2+</sup>, and (d) Cu<sup>2+</sup> (scale bars= 100 nm).

merization and mineralization, silica will deposit onto the surface of twisted nanohelix and in this way chiral nanostructures are successfully transcribed into silica materials (Figure 4). X-ray energy dispersive spectroscopy (EDS) provided in Supporting Information Figure S4 shows the material is composed of Si and O. Moreover, soft assemblies are considered to be superior templates in directing nanomaterial synthesis owing to their tunability in shape, size and superstructures. Herein, calcium-cholate supramolecular nanohelices are found to be varied in diameter, pitch, pitch-to-diameter ratio and intertwining extent which can be conveniently modulated by SC/Ca<sup>2+</sup> molar ratio (see Supporting Information, Figure S5). It is therefore hopeful that these supramolecular helices can be exploited to create one-dimensional helical silica with controllable size and shape.

It is worthwhile that metal-cholate supramolecular self-assembly is expected to be a general route toward one-



**Figure 6.** a), b) TEM and c) SEM images of ZnS semiconductor helical nanotubes.

dimensional nanohelix. Herein we have demonstrated that a series of metal ions can be utilized to fabricate 1D metal-cholate supramolecular helix. The TEM images in Figure 5 give convinced evidence of well-defined nanohelices constructed by sodium cholate and various metal ions including  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cu}^{2+}$ . All these supramolecular assemblies exhibit a twisted shape of nanoribbons. The incorporation of different metal centers are anticipated to endow novel and unique functionalities to supramolecular nanohelices in diverse subjects such as material science, biological field, catalysis, sensors, and photoluminescence devices. As shown in Figure 6, zinc-cholate supramolecular helices are transformed into helical zinc sulfide semiconductor material.

In this strategy, 1D helical zinc sulfide nanotubes was prepared via self-templating approach in which metal ions can serve as both inorganic precursor and constituent of template. With the addition of  $\text{Na}_2\text{S}$ , helical ZnS semiconductor nanotubes can be directly deposited from zinc-cholate supramolecular nanohelices. TEM and SEM images provide strong evidence of zinc sulfide helical nanotubes with external diameters of 30–70 nm, inner diameters 10–50 nm and helix pitches of about 50 nm (Figure 6). The structural size and morphology of ZnS helix is in good agreement with zinc-cholate nanohelices. The atomic ratio of Zn to S in these nanotubes is determined by EDS to be roughly 1:1 (Supporting Information, Figure S6). It is assumed that zinc ion inside zinc-cholate nanohelix will diffuse toward nanohelix surface in the presence of bulk  $\text{Na}_2\text{S}$ , leading to the formation of hollow ZnS nanotubes. To the best of our knowledge, this is the first report of zinc sulfide helical nanotubes. It is hopeful that series of helical inorganic nanomaterials can be designed based on MCSS. Further study is still undergoing in our lab.

To conclude, a facile route to fabricate metal-driven one-dimensional nanohelices has been reported. In a typical case, well-defined right-handed helical nanoribbons constructed by calcium-cholate supramolecular self-assembly are systematically described. The cooperative effect of multiple weak interactions (i.e., hydrogen bond, coordinating interaction and hydrophobic effect) is proposed to account for the hierarchical nanohelices. By virtue of metal-cholate supramolecular systems, we have succeeded to prepare  $\text{SiO}_2$  and ZnS helical nanomaterials via two distinct strategies, sol–gel process and self-templating method. It is believed that metal-cholate supramolecular systems are appealing soft templates for designing inorganic helical materials.

We also anticipate that this study may shed a light on the fabrication of hierarchical nanostructures, especially one-dimensional helical architectures, and lead to a comprehensive understanding of natural approach to generate supramolecular architectures with predefined size, topology, stereochemistry, hierarchy, and shape and to reveal some complex processes in biological systems, such as gallstone formation.

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**Supporting Information Available:** Experimental section, FT-IR, ESI-MS spectra, EDS, and TEM images of nanohelices are presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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