Short Communication

β-cyclodextrin mediated construction of porous helical nanoribbons from oligoaniline derivatives

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Abstract

A novel supramolecular self-assembly nanostructure of porous helical nanoribbons (PHNRs) was developed. PHNRs from oligoaniline derivatives were fabricated through the chemical oxidation of aniline in an *i*-propanol/water mixture as mediated by *β*-cyclodextrin (*β*-CD). The role of *β*-CD was considered vital through the modulation of the addition time point of *β*-CD and the molar ratio of *β*-CD/aniline. In addition, at the early stage of polymerization, the host-guest complex between oligoaniline and *β*-CD was formed, which was involved in the initial supramolecular assembly process. However, with the reorganization of the oligoaniline assemblies during the polymerization time, the abscission of *β*-CD from the helical nanoribbons was observed, which eventually induced the formation of PHNRs. We believe the supramolecular host-modulated assembly strategy presented herein will be instructive for the fabrication of porous supramolecular nanostructures.

Keywords: *β*-CD, oligoaniline derivatives, supramolecular assembly, porous helical nanoribbons

INTRODUCTION

Supramolecular nanostructures have emerged as promising materials in the field of drug delivery[1], catalysis[2], sensing[3], and luminescence[4]. In their construction, the self-assembly strategy has been

extensively used since it can afford unique hierarchical nanostructures through noncovalent interactions, such as hydrogen bonding, van der Waals interactions, and electrostatic interactions[5]. Owing to the reversible and dynamic nature of the noncovalent interactions, supramolecular nanostructures can be manipulated by other external stimuli, including solvent[6], light[7], and even extra components, such as host molecules[8], which can be employed to induce the reorganization of guest molecules and promote the achievement of diverse supramolecular nanostructures.

Cyclodextrin (CD), a typical host molecule with a hydrophobic cavity, is considered as an excellent candidate for the regulation of supramolecular structures. Sun and co-workers reported the photo-controlled morphology switch from nanoparticle to nanotube through the modulation of a *β*-CD-based host-guest complex[9]. It was also demonstrated that, during the RAFT dispersion polymerization of styrene, the introduction of CD can direct the controllable fabrication of spheres, worms, lamellae, and nanotubes[10]. However, the development of novel nanostructures, such as porous ones, remains a challenge.

Recently, we reported the fabrication of supramolecular helical nanoribbons from oligoaniline derivatives via the chemical oxidation of aniline in an alcohol/water mixture[11]. Inspired by the controllable self-assembly capability of oligoaniline, and taking into account that *β*-CD is suitable for the inclusion of oligoaniline, a novel supramolecular self-assembly nanostructure of porous helical nanoribbons (PHNRs) was developed. PHNRs from oligoaniline derivatives were fabricated through the chemical oxidation of aniline in an *i*-propanol/water mixture as mediated by *β*-cyclodextrin (*β*-CD). At the early stage of the polymerization of aniline, a supramolecular complex was formed between *β*-CD and tri-aniline derivatives and involved in the initial assembly of spindle nanoflakes. However, according to the morphological evolution of *β*-CD mediated oligoaniline assemblies, the combination of *β*-CD abscission from the helical nanoribbons and the reorganization of oligoanilines along with polymerization time eventually led to the formation of PHNRs [Scheme 1].

RESULTS AND DISCUSSION
β-CD mediated construction of PHNRs
According to our previous report, helical nanoribbons can be prepared from oligoaniline derivatives through the chemical oxidative polymerization of aniline in an *i*-propanol/water mixture, where right- or left-handed helical nanoribbons of oligoaniline derivatives can be obtained by controlling the *i*-propanol content of the mixed solution[11]. Inspired by the controllable self-assembly performance of oligoaniline, and taking into account that oligoaniline can form a host-guest inclusion complex with *β*-CD, *β*-CD was employed to further manipulate the supramolecular assembly process of oligoaniline. Specifically, aniline was oxidized using ammonium peroxodisulfate (APS) as an oxidant in an *i*-propanol/water mixture, where the *i*-propanol content at 40% was chosen as a typical example for the fabrication of helical nanoribbons of oligoaniline[12]. At the point of 4 min of polymerization, *β*-CD, of which the molar amount was kept the same as aniline, was added, and the reaction mixture was left for 12 h at 25 °C. After that, the product was centrifuged and washed with deionized water. Finally, the resulting solid was dried to afford the target black powder.

The morphology of the synthesized product was investigated using field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). As shown in Figure 1A-C, in the absence of *β*-CD, highly uniform and dense 1D helical nanoribbons with several microns in length were observed in both FESEM and TEM images, which is in high agreement with our previous report[11]. By contrast, surprisingly, when mediated by *β*-CD, the helical nanoribbons obtained were porous [Figure 1D-F and Supplementary Figure 1], with an almost unchanged size. These results indicate that *β*-CD participated
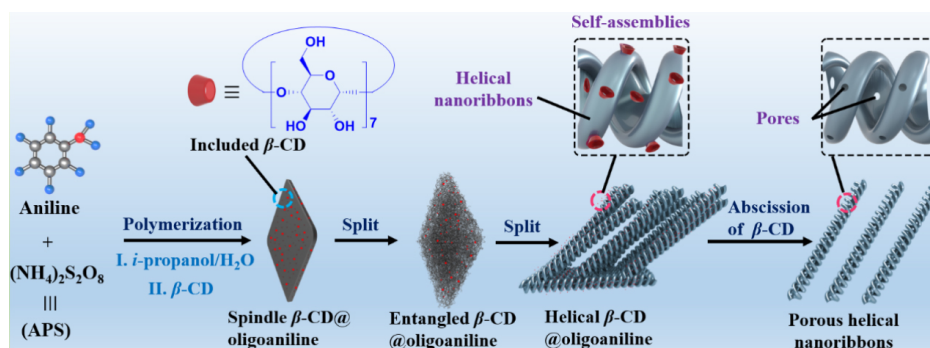
Scheme 1. Schematic illustration of the β-CD mediated formation of porous helical nanoribbons. The chemical structures of aniline and ammonium peroxodisulfate, as well as β-cyclodextrin, are presented. β-CD: β-cyclodextrin.
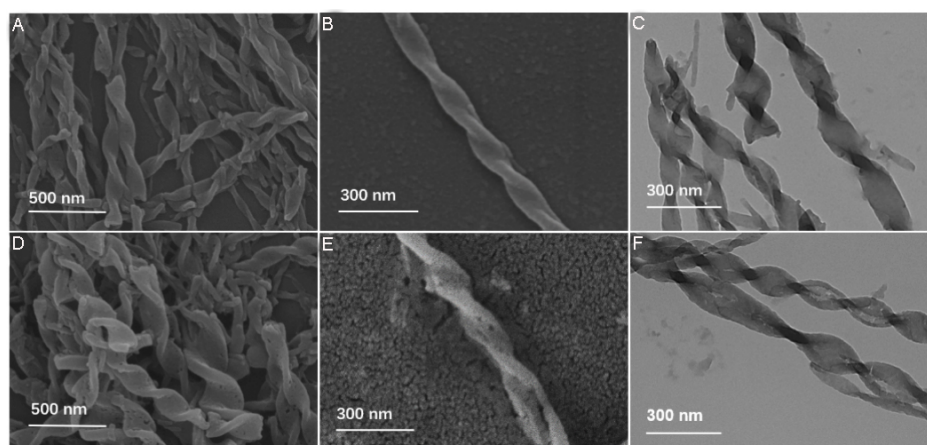

Figure 1. (A-E) FESEM and (C and F) TEM images of helical nanostructures synthesized (A-C) in the absence of β-CD and (D-F) in the presence of β-CD. FESEM: Field emission scanning electron microscope; TEM: transmission electron microscope; β-CD: β-cyclodextrin.

in the assembly process of oligoaniline and played a dominating role in the formation of porous helical nanoribbons (PHNRs).

The time point for the addition of β-CD during the polymerization of aniline was considered to be important for the fabrication of PHNRs. To verify this assumption, synthesis experiments were carried out on the modulation of the addition time of β-CD. The morphologies of the products obtained under different conditions were investigated by TEM. Interestingly, helical nanoribbons bearing large and relative uniform pore channels were observed upon the addition of β-CD at 4 min of polymerization [Figure 2B]. By contrast, the introduction of β-CD at shorter (1 min) [Figure 2A] and longer polymerization times (9 min) [Figure 2C] showed helical nanoribbons featuring small pore size and nonporous morphologies, respectively. According to the above results, it is logical to speculate that the dominating product at 1, 4, and 9 min of polymerization was different, and β-CD exhibited stronger binding capability towards the product formed at 4 min of polymerization of aniline. This deduction was supported by the UV-vis experiments. As shown in Supplementary Figure 2, the addition of 1 equiv. of β-CD at 1 min polymerization induced the observation of a singlet peak at 281 nm, which was ascribed to the monomer aniline. Remarkably, the absorption peak at 281 nm experienced an obvious decrease along with the appearance of a new peak at 374 nm after the addition of 1 equiv. of β-CD at 4 min polymerization. We assigned this new peak as oligoaniline[12]. The addition of β-CD at a longer polymerization time (9 min) led to the slight diminishment
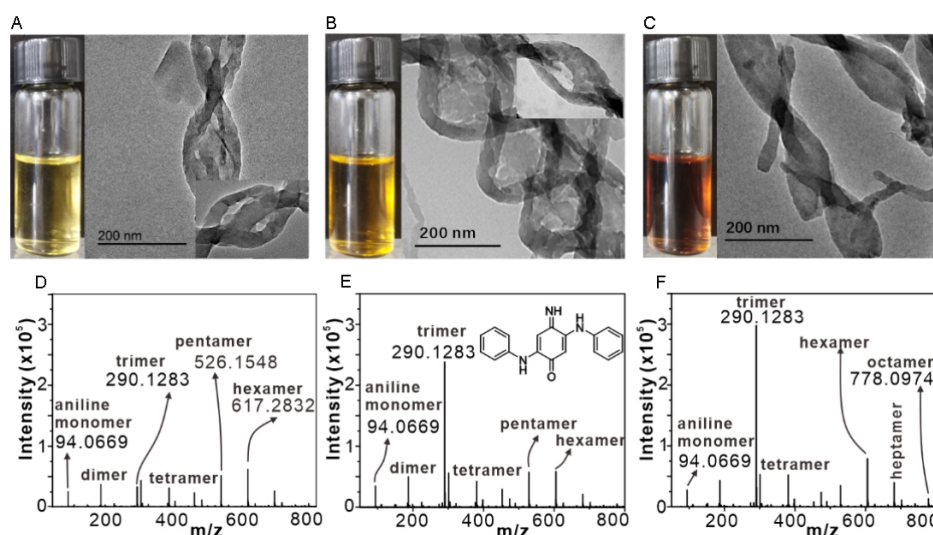
Figure 2. (A-C) (Left) Photographs of the polymerization mixture at the polymerization times of: (A) 1 min; (B) 4 min; and (C) 9 min. (Right) TEM images of β-CD mediated nanostructures assembled from oligoaniline for 12 h with the addition of β-CD at different polymerization times: (A) 1 min; (B) 4 min; and (C) 9 min. (A and B) (Inset) Magnified TEM images. (D-F) High-resolution mass spectra (HRMS with ESI mode) of the polymerization mixture at the polymerization times of: (D) 1 min; (E) 4 min; and (F) 9 min. Note that the aniline monomer and its oligomers (oligoaniline derivatives), such as dimer, trimer, tetramer, pentamer, hexamer, heptamer, and octamer, are carefully labeled in (D-F). TEM: Transmission electron microscope; β-CD: β-cyclodextrin; HRMS: high-resolution mass spectrometry.

of the aniline absorption and gradual enhancement of oligoaniline. This result not only illustrates the binding events between β-CD and oligoaniline formed at different polymerization times but also substantiates the importance of the additional time point of β-CD to the construction of porous nanostructures. Thus, the colors of the solutions obtained at different polymerization stages were also observed. The color changed from pale yellow to dark brown over time, as shown in Figure 2A-C (inset), which clearly confirmed the different polymerization degrees.

To further verify the possible structure of the oligoaniline obtained at different polymerization times, the mixtures from different polymerization times were investigated using high-resolution mass spectrometry (HRMS with ESI mode; Figure 2D-F and Supplementary Figure 3, Supplementary Table 1). The mass spectrum showed multiple ion peaks consistent with various oligoaniline derivatives for the sample that was polymerized for 1 min [Figure 2D]. Typically, an intense ion peak at m/z = 290.1283, corresponding to the mono-charged species of [tri-aniline+H]$^+$, was detected in addition to the free aniline ion peak at m/z = 94.0669. The ion peak of [tri-aniline+H]$^+$ evolved into the most intense one after 4 min of polymerization, indicating that the tri-aniline derivative $C_{18}H_{16}N_4$ was the main component at this polymerization stage [Figure 2E]. However, when the polymerization time reached 9 min, an ion peak at m/z = 778.0974, which could be assigned to the octa-aniline derivative, appeared [Figure 2F]. Based on the above results, we assume that at the early polymerization time (1 min), a lower amount of tri-aniline oligomer was produced. When β-CD was added at this time point, a lower degree of β-CD/tri-aniline oligomer complex was formed, leading to less involvement of β-CD in the polymerization process.

At the polymerization time of 4 min, a higher amount of tri-aniline oligomer was obtained, which led to the relative concentrated formation of β-CD/tri-aniline oligomer complex and, thus, a higher engagement of β-CD during the polymerization. However, at a longer polymerization time (9 min), the product with a higher polymerization degree, namely the octa-aniline derivative, was too bulky to interact with β-CD,

which led to a lower engagement of β-CD as well. In addition, the molar ratio of β-CD/aniline was modulated. As shown in Supplementary Figure 4, increasing the amount of β-CD led to a greater number of pores or even disruption of the helical nanoribbons. Above all, the involvement of β-CD in the initial polymerization process was considered to be the key factor for obtaining porous helical ribbons.

Morphological evolution of PHNRs
As discussed above, PHNRs with large pores were observed upon the addition of β-CD after 4 min polymerization of aniline; therefore, to clarify the role that β-CD played in the fabrication of PHNRs, this optimal condition was selected to monitor the formation process of PHNRs [Figure 3 and Supplementary Figure 5]. Figure 3 shows the nanostructures assembled from β-CD mediated oligoaniline derivatives at different time intervals. Spindle nanoflakes could be obtained after 1 h of polymerization. It is worth noting that the nanoflakes started to split and afford the nanofiber structures after 3 h. When the polymerization time was extended to 5 or 9 h, clusters of twisted nanoribbons, composed of entangled nanoribbons, were observed. Surprisingly, helical nanoribbons bearing multiple pore channels, namely PHNRs 100-150 nm in width and 200-250 nm in average pitch, were formed after 12 h of polymerization. As evidenced by the SEM and TEM images, we measured the pore sizes of the porous helical nanoribbons in the range of 15-35 nm. Based on these observations, we hypothesize that β-CD was involved in the early polymerization process to a certain extent and directed the formation of PHNRs through the abscission from the helical nanoribbons.

To investigate the size effect of the β-CD on the formation of the porous helical nanoribbons, we selected its analogs, α-CD and γ-CD, to mediate the nanostructure formation under the same conditions. As shown in Supplementary Figure 6, the addition of 1 equiv. of α-CD at the 4 min polymerization time point along with polymerization for 12 h induced the observation of porous helical nanoribbons with smaller pore sizes compared to those obtained by β-CD. In contrast, neither porous character nor helical nanostructures were detected in the presence of 1 equiv. of γ-CD. Taken together, these observations demonstrated that α-CD and β-CD displayed similar binding affinity towards the oligoaniline, while negligible binding existed in the case of γ-CD due to its larger size. However, γ-CD also damaged the polymerization of aniline, which eventually led to the disappearance of helical nanoribbons.

To investigate the helical sense discrepancy of the helical nanostructures, we performed circular dichroism experiments in an *i*-propanol/water solvent mixture [Supplementary Figure 7]. The helical nanoribbons formed in the absence of β-CD showed a positive Cotton effect at 202 nm, which is in agreement with the literature[11]. By contrast, the porous helical nanoribbons mediated by β-CD exhibited a positive Cotton signal with a blue-shift at 196 nm. This finding demonstrates that the emergence of the porous features did not affect the helical sense of the porous nanoribbons but enhanced the intermolecular π-π interaction to a certain extent.

Formation mechanism of PHNRs
To test the above formation hypothesis, fourier-transform infrared spectroscopy (FTIR) measurements were conducted. As shown in Figure 4, the spectrum of β-CD showed a typical -OH band at 3421 cm^{-1} (Figure 4F, left), and the spectrum of helical nanoribbons assembled from oligoanilines, obtained with 12 h polymerization in the absence of β-CD, showed two characteristic bands at 1572 and 1509 cm^{-1}, corresponding to C=C stretching vibration in quinonoid and benzenoid rings, respectively. In addition, the peak located around 1352 cm^{-1} could be ascribed to the C-N stretching mode of benzoquinone imine (Figure 4A, left). It is worth noting that, after the introduction of β-CD into the oligoaniline solution for 1 h, the three mentioned FTIR adsorption peaks of oligoaniline were slightly shifted to lower wavenumbers with reduced intensity compared to free oligoaniline (Figure 4B, left), indicating the establishment of a supramolecular complex between oligoaniline and β-CD. However, with the extension of the
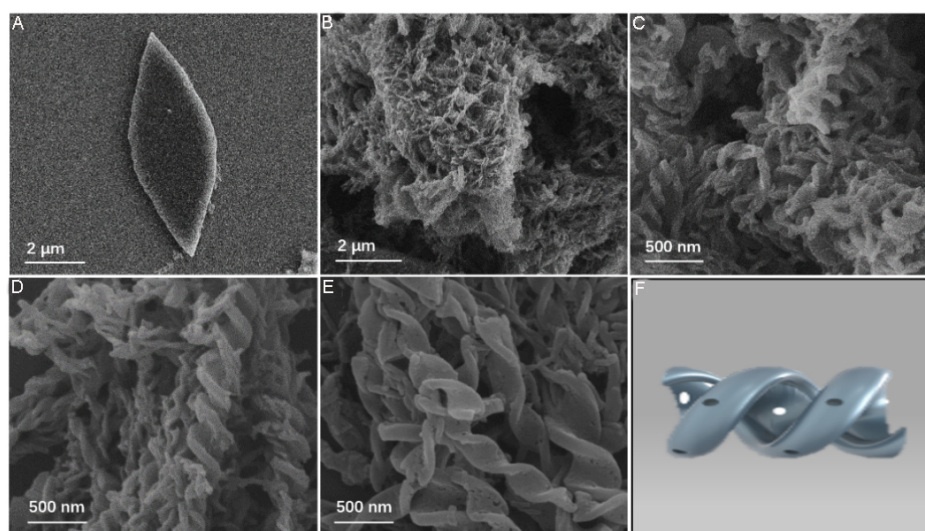
Figure 3. FESEM images of the nanostructures assembled from *β*-CD mediated oligoaniline derivatives at different polymerization times: (A) 1 h; (B) 3 h; (C) 5 h; (D) 9 h; and (E) 12 h. (F) A cartoon image of PHNR. FESEM: Field emission scanning electron microscope; *β*-CD: *β*-cyclodextrin; PHNR: porous helical nanoribbon.
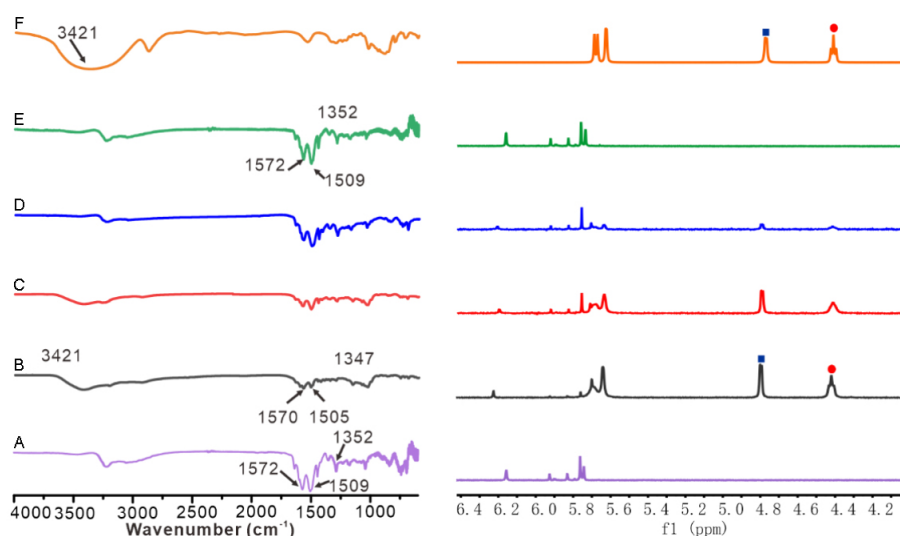

Figure 4. (Left) FTIR spectra and (Right) selected ^{1}H NMR spectra of (A) oligoanilines obtained with 12 h polymerization in the absence of *β*-CD. *β*-CD mediated polymerization product at various polymerization times: (B) 1 h; (C) 3 h; (D) 5 h; and (E) 12 h. (F) *β*-CD. FTIR: Fourier-transform infrared spectroscopy; NMR: nuclear magnetic resonance; *β*-CD: *β*-cyclodextrin.

polymerization time, the specific bound bands of both oligoaniline and *β*-CD started to diminish (Figure 4C and D, left) and completely disappeared after 12 h (Figure 4E, left). Moreover, the characteristic bands of free oligoaniline reappeared simultaneously, which indicated the disassociation of the *β*-CD/oligoaniline complex.

To further disclose the underlying mechanism of the *β*-CD mediated formation of PHNRs, the ^{1}H NMR spectra of *β*-CD, helical nanoribbons assembled from oligoanilines obtained with 12 h polymerization in the absence of *β*-CD, and the *β*-CD mediated polymerization product at various polymerization times in deuterated DMSO solution were obtained. Note that the samples taken from the polymerization system

were centrifuged and washed with water to remove free aniline, APS, and *β*-CD. As shown in Figure 4 (right), when *β*-CD was added into the polymerization system for 1 h, the hydroxyl protons of *β*-CD, located in the range of 4-5 ppm, from the resulting product experienced a slight downfield shift in comparison with that of free *β*-CD, an indication of the formation of the *β*-CD/oligoaniline complex. However, with the increase of the polymerization time, the signals arising from *β*-CD were largely attenuated for the *β*-CD mediated polymerization product and completely disappeared after 12 h. The above results further verify the abscission of *β*-CD from the oligoaniline assemblies with the extension of polymerization time, which was considered the crucial reason for the formation of PHNRs.

Taken together, the formation mechanism of the PHNRs was proposed as follows: A supramolecular complex was formed between *β*-CD and tri-aniline at the early stage of polymerization and involved in the assembly of spindle nanoflakes [Figure 3A]. However, with the reorganization of the oligoaniline assemblies over time, the abscission of *β*-CD from the helical nanoribbons was observed, which eventually induced the formation of PHNRs.

CONCLUSIONS

We describe the *β*-CD mediated fabrication of porous helical nanoribbons via the chemical oxidation of aniline in an *i*-propanol/water mixture. The effective formation of the *β*-CD/oligoaniline complex at the early stage of aniline polymerization was demonstrated, which was subsequently involved in the assembly of spindle nanoflakes. However, with the reorganization of the oligoaniline assemblies over time, the abscission of *β*-CD from the helical nanoribbons was observed, which eventually induced the formation of PHNRs. We believe the supramolecular host-modulated assembly presented herein may provide an alternative approach for the construction of unique porous nanostructures.

DECLARATIONS

Authors' contributions
Implemented synthesis, conducted morphology characterization and analyzed data: Liu SY
Performed data analysis, wrote and revised the manuscript: Sun QQ
Performed synthesis: Hang PY
Performed data analysis, wrote and revised the manuscript: Sun XH
Performed morphology characterization: Zhou CQ
Performed data analysis and revised the manuscript: Han J
Revised the manuscript: Guo R

Availability of data and materials
The data supporting this article have been included as part of the Supplementary Materials.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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