



Single-handed helical carbonaceous nanotubes prepared using a pair of cationic low molecular weight gelators



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ABSTRACT

We design a facile route to obtain enantiopure carbonaceous nanostructures, which have potential application as chiral sensors, electromagnetic wave absorbers, and asymmetric catalysts. A pair of cationic low molecular weight gelators was synthesized, which were able to self-assemble into twisted nanoribbons in ethanol at a concentration of 20 g L^{-1} at 25°C . Single-handed helical 3-aminophenol-formaldehyde resin nanotubes with optical activity were prepared using the self-assembly of the low molecular weight gelators as templates. After carbonization, single-handed helical carbonaceous nanotubes were obtained and characterized using circular dichroism, wide-angle X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. The results indicate that the walls of the nanotubes are amorphous carbon. Moreover, the left- and right-handed helical nanotubes exhibit opposite optical activity.

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1. Introduction

With the development of single-walled carbon nanotubes, carbonaceous nanostructures with helical morphology and optical activity have attracted much attention for their potential application in asymmetric catalysis, enantioseparation, electromagnetic absorption, and chiral optics [1–3]. Although several synthetic approaches have been developed for the preparation of helical carbonaceous nanomaterials [4,5], the fabrication of enantiopure carbonaceous nanostructures is still a challenge. To date, three methods have been developed for the production of single-handed helical carbonaceous nanotubes: the first method involves the calcination and removal of silica from single-handed helical polybissilsesquioxane nanotubes [6,7], and the second involves the pyrolysis of single-handed helical polypyrrole nanotubes [8]. It has been reported that cross-linked phenolic resins are a promising carbon source because of their high carbon conversion yield, thermal stability, and mechanical strength [9,10]. Therefore, it is beneficial to prepare enantiopure carbonaceous nanostructures from enantiopure cross-linked polymers. Recently, we developed the third production method, the carbonization of 3-aminophenol-formaldehyde resin (APFR) nanotubes, which were prepared through a supramolecular templating method using the

self-assembly of $-\text{COOH}$ terminated compounds as the templates [11]. Static electric interactions and hydrogen bonding were proposed to drive the morphological transfer from organic self-assemblies to the APFR nanotubes. Herein, we show that APFR nanotubes could also be prepared using the self-assembly of cationic low molecular weight gelators as the templates. After carbonization, single-handed helical carbonaceous nanotubes with optical activity were obtained.

2. Experimental

2.1. Materials

Compounds L-1 and D-1, whose molecular structures are shown in Fig. 1, were synthesized according to the literature [12]. 3-aminophenol, formaldehyde aqueous solution (37–40 wt%) and anhydrous methanol were obtained from Aldrich.

2.2. Synthesis

2.2.1. Synthetic procedure for APFR nanotubes

L-1 or D-1 (40 mg) and 3-aminophenol (100 mg) were dissolved in 20 mL of anhydrous methanol/water (1:1 v/v) at 60°C . After 10 min, 0.3 mL of an aqueous solution of formaldehyde were added into the solution and the reaction mixture was stirred for 2 h at 60°C , followed by aging at 80°C for 2 h. The resultant yellow

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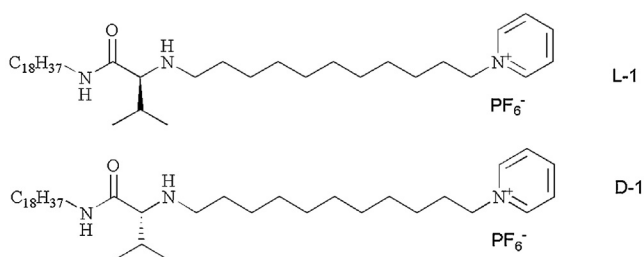


Fig. 1. Molecular structures of the low molecular weight gelators.

precipitate was filtered and dried to yield as-prepared APFR nanotubes, which were extracted with 60 mL of anhydrous ethanol for 48 h to remove the organic low molecular weight compounds.

2.2.2. Synthetic procedure for helical carbonaceous nanotubes

The above obtained APFR nanotubes were carbonized at 900 °C for 4 h with a heating rate of 3.0 °C/min in Ar. After naturally cooling to room temperature, the carbonaceous nanotubes were obtained.

2.3. Characterization

Field-emission scanning electron microscopy (FE-SEM) was performed using a Hitachi 4800 instrument at 3.0 kV. Transmission electron microscopy (TEM) images were obtained using an FEI TecnaiG220 at 200 kV. Wide-angle X-ray diffraction patterns were collected with an X'Pert-Pro MPD X-ray diffractometer using Cu K α radiation (1.542 Å). Raman spectra were recorded using a Jobin Yvon Horiba HR 800 LabRAM confocal microprobe Raman system with Ar laser excitation (514.5 nm) and a power of 10 mW. Ultraviolet-visible (UV-vis) and circular dichroism (CD) spectra were measured using an AVIV 410 spectrophotometer with a 1.0 nm bandwidth.

3. Results and discussion

Low molecular weight gelators (LMWGs) derived from amino acids have attracted much attention owing to their potential applications for medical use [13–15]. Moreover, they can self-assemble to various helical nanostructures, which have been

used as templates to prepare helical and chiral nanomaterials [16–18]. Herein, L-1 and D-1 can self-assemble into left- and right-handed twisted nanoribbons in anhydrous ethanol at a concentration of 20 g L⁻¹ at 25 °C (Fig. 2). The CD and UV spectra of the LMWGs are shown in Fig. 3. Two absorption bands at approximately 200 nm and 260 nm appear in the UV spectra, which are mainly attributed to the absorption of carbonyl and pyridine groups, respectively. Essentially opposite CD signals are observed for the L-1 and D-1 organogels in ethanol at a concentration of 20 g L⁻¹. For L-1, the first positive signal at $\lambda = 275$ nm indicates a clockwise stacking of the aromatic rings. However, for D-1, the first negative signal at $\lambda = 280$ nm indicates an anti-clockwise stacking of aromatic rings.

Single-handed helical APFR nanotubes have been prepared using the self-assembly of LMWGs as templates. The FE-SEM and TEM images of the helical APFR nanotubes are shown in Fig. S1. Left- and right-handed helical APFR nanotubes, denoted as M-APFR and P-APFR, were obtained using L-1 and D-1, respectively. The outer diameters, inner diameters, and helical pitches of the APFR nanotubes are 100–150 nm, 30–50 nm, and 800–1000 nm, respectively. Carbonaceous nanotubes, denoted as M-C and P-C, were obtained after carbonization of M-APFR and P-APFR, respectively, at 900 °C for 4 h. The FE-SEM and TEM images of the carbonaceous nanotubes are shown in Fig. 4. The single-handed helical morphologies are basically maintained. The outer and inner diameters of the carbonaceous nanotubes are 50–100 nm and 20–30 nm, respectively, which indicated thermal shrinkage of the resin nanotubes during pyrolysis. Additionally, disordered micropores can be identified within the walls of the carbonaceous nanotubes (Fig. 4c and d), which are also believed to be formed during pyrolysis. The results shown here indicate that cationic templates derived helical APFR nanotubes are promising carbon sources to fabricate helical carbonaceous nanotubes. Besides, the carbonaceous nanotubes with micropores within the walls can be used as absorbents or catalyst carriers [19,20].

The Raman spectrum for M-C is shown in Fig. S2. The G and D bands are observed at 1600 cm⁻¹ and 1358 cm⁻¹, respectively. The I_G/I_D ratio for M-C is approximately 0.64, indicating that the carbon is amorphous or that the crystalline size in the sample is very small [21,22]. The wide-angle X-ray diffraction pattern for M-C is shown in Fig. S3. Two broad peaks are identified at 2θ values of 23.1° and 43.8°, corresponding to the (002) and (100) planes for graphite, respectively. These results imply that no large crystalline domains are present in the sample.

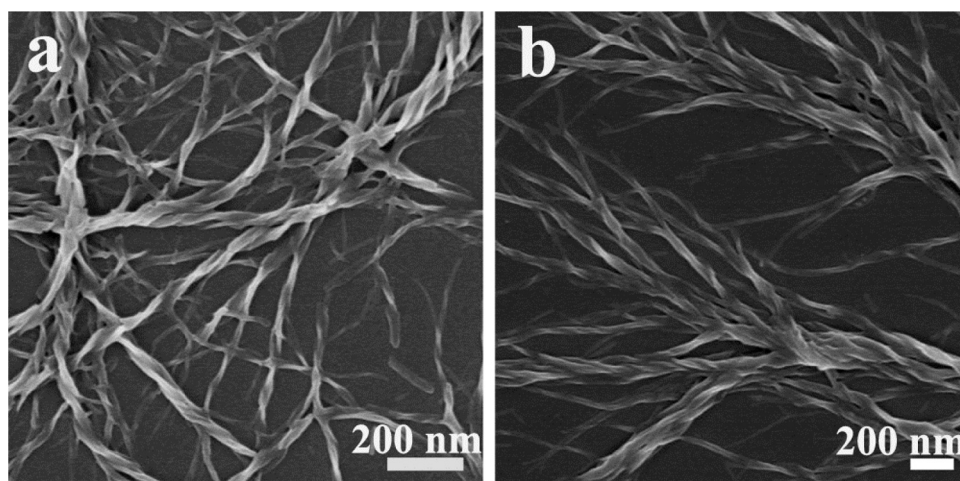


Fig. 2. Field-emission scanning electron microscopy images of xerogels of (a) L-1 and (b) D-1 prepared at a concentration of 20 g L⁻¹ in anhydrous ethanol.

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