A Facile Route to Carboxylated Carbon Nanofibers and Their Functionalization by Robust Octasilsesquioxanes via conjugated linkage

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Table of Contents:

1. The information about the chemicals and instruments

2. Synthesis of octa-aminophenylsilsesquioxane (OASQ)

3. The effect of sonication condition

4. FTIR spectra of nanofibers. (a) tNF, tNF-u1, and tNF-u2. (b) pNF, pNF-u1, and pNF-u2. (Fig. S1)

5. FT-IR spectrum of tNF-(COOH)_{n2} heated at 120 °C for 2 h. (Fig. S2)

6. TGA analysis of nanofibers after sonication. (Fig. S3)

7. Auger chemical composition analysis of nanofibers. (Fig. S4)

8. Photoluminescence emission spectra. (Fig. S5)

9. XRD patterns of nanofibers. (Fig. S6)

10. TEM images of nanofibers: (a) tNF, (b) pNF, (c) tNF-u1, (d) pNF-u1, (e) tNF-u2, (f) pNF-u2. (Fig. S7)

11. TEM images of nanofibers participated in the F-C reaction with various amount of oxalyl chloride. (Fig. S8)

12. Digital photographs of dispersion of nanofibers in THF. (Fig. S9)

13. Nitrogen adsorption/desorption isotherms of nanofibers. (Fig. S10)

14. TEM image of associated floating skims collected from nanofibers after sonication.

(Fig. S11)

15. Raman spectra of tNF-u1, pNF-u1, tNF-u2 and pNF-u2. (Fig. S12)

16. Reference for the Supporting Information

1. The information about the chemicals and instruments

Hydrazine hydrate (80%), THF, DMF, ethyl acetate, hexane, chloroform and hydrochloric acid were purchased from the Tianjin Kermel Chemical Reagents Development Centre. FeCl₃, active charcoal powder, oxalyl chloride and aluminium trichloride were of analytical reagent grade and purchased from Aladdin Chemistry Co., Ltd. THF and chloroform was dried over molecular sieves and distilled over CaH₂. DMF was dried over molecular sieves.

¹H and ²⁹Si nuclear magnetic resonance (NMR) spectra were investigated on Bruker AM-400S (400 MHz) spectrometer using tetramethylsilane (TMS) as internal standard and dimethylsulfoxide-d as solvent. FTIR spectra were recorded on a TENSOR27 Fourier transform spectrophotometer and measured at a 0.9 cm⁻¹ resolution using KBr pellets. Raman spectra were measured with a laser Raman microscope (LabRAM Aramis, HORIBA Jobin Yvon) using a wavelength of 632.8 nm as the excitation source. To focus the light on the sample, a microscope objective with 10× magnification was employed, and the laser power density on the sample was kept below 30 W cm² To avoid any sample modification. Spectra were collected from different fibers of a given sample to check the sample homogeneity. Elemental compositions were obtained from CHNS elemental analysis (vario EL III). The thermogravimetric analysis (TGA) measurement was performed with a TG209F3 thermogravimetric analyzer over a temperature range of between 30 and 800 °C at a heating rate of 10 °C/min under nitrogen. Transmission electron microscopy (TEM) images were obtained with a JEM-100CX II microscope at an acceleration voltage of 100 kV. The Ultraviolet/Visible (UV/Vis) absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer at room temperature. The photoluminescence emission spectra were recorded with a Hitachi F-4600 spectrometer and detected at 275 nm. All measurements were performed at room temperature. Sonication was conducted at 20 kHz with an adjustable power using a Rotary ultrasonic focusing treatment apparatus (NPC, NewPower ultrasonic Electronic Equipment Co., Ltd).

2. Synthesis of octa-aminophenylsilsesquioxane (OASQ)

Octa(nitrophenyl)silsesquioxane (ONSQ) was synthesized in our laboratory.¹ ONSQ (0.5g, 0.358mmol, $-NO_2$ 2.87 mmol), FeCl₃ (10 mg), and 0.4 g active charcoal powder were charged into a three-necked 100 mL round-bottomed flask. THF (20 mL) was then added to the flask. The solution was stirred and heated to 60 °C under purified nitrogen. ^{1,2} Hydrazine hydrate (2 mL)

was added dropwise into the mixture. The reaction was continued for 5 h, and then the solution was cooled and filtered through Celite. The filtrate was combined with 20 mL of ethyl acetate and washed with H₂O four times. The organic layer was dried over MgSO₄ and poured into 200 mL hexane. The white precipitate was collected by filtration. The product was redissolved in the mixture of 9 mL THF and 15 mL ethyl acetate, and reprecipitated into 150 mL hexane. The obtained powder was dried in vacuum. FTIR (KBr): 3369, 3220 (w; N–H), 1119 cm⁻¹ (s; Si–O–Si); ²⁹Si NMR (δ , ppm): –70.0, –77.5; ¹H NMR (DMSO–*d*6,) (d, ppm): 7.8–6.2 (b, 2.0H), 5.2–3.7 (b, 1.0H).

3. the effect of sonication condition

Sonication treatment of CNFs

CNFs (tNF or pNF, 100 mg) was dispersed in 100 mL of chloroform; by a 60-min sonication treatment with 100 W (u1). The resulting product was collected by filtration, denoted as CNF-u1 (tNF-u1 or pNF-u1), immersed in diluted hydrochloric acid for overnight and washed with water and ethanol. It was then dried under vacuum at 75 °C for 48 h. When the time of sonication was set to 10 min with 60 W (u2), the resulting product was denoted as CNF-u2 (tNF-u2 or pNF-u2).

The carbonyl group peak intensity of CNF-u1 and CNF-u2 at 1722 cm⁻¹ has seen very little change (Fig. S1a,b). It indicates that the number of carboxyl groups is nearly constant before and after sonication. There were early reports³⁻⁵ that carbon nanotubes or nanofibers could react in specific atmosphere or solvent through a simple mechanochemical reaction such as ball-milling and ultrasound at room temperature to introduce functional groups like thiol, hydroxy, amide, carbonyl, chlorine, etc. onto the surface. However, our work suggests that ultrasonic do not make the number of carboxyl groups increase under inert atmosphere with respect to that of Friedel-Crafts reaction.

The TEM images of tNF and pNF with the typical tubular microstructure show that the nanofibers are long and straight with smooth surface (Fig. S7a,b). The average thickness of the wall is approximately 30 nm for tNF and 50 nm for pNF. The shell of tNF-u1 and pNF-u1 treated with 100w for 60 min is thinner than the pristine tNF and pNF, respectively (Fig. S7c,d). There is an obvious decrease in the diameter as well. We observed that some translucent films, like oil slicks, were floating about on the solvent. The TEM images of the skims collected indicates that the individual graphene flakes stack together to form larger size platelets (Fig. S11). The changes

of diameter and wall thickness are probably due to the disruption and stripping of the outer graphitic layers after strong sonication. Note that the wall thickness of tNF-u1 becomes nonuniform and the diameter varies in different positions. Instead, the wall thickness of pNF-u1 is uniform, and diminishes to 15nm. For tNF-u2 and pNF-u2 treated with 60w for 10 min, the diameter is 100 nm and 150 nm – nearly the same as that of the corresponding starting nanofibers (Fig. S7e,f).

Fig. S3a shows the TGA curves of the tNF, tNF-u1 and tNF-u2 samples. Their char yields at 850 °C are 96.7%, 93.5% and 97.3%, respectively. All three display excellent thermal stability in nitrogen, due to the orderly structure and high degree of crystallization. For tNF-u1, the greater weight loss of 6.5% is probably ascribed to a more serious disruption of the nanofibers with the radical sonication posing more defects. The char yields of pNF, pNF-u1 and pNF-u2 at 850 °C are 98.3%, 95.2% and 98.4%, respectively (Fig. S3b).

For the tNF, tNF-u1 and tNF-u2, the value of I_D/I_G ratio is 1.87, 2.02 and 1.94, respectively (Fig. S11). The tNF-u1 exhibites a significant change in the amount of defect sites. This suggests that the sonication with 100w for 60 min is sufficiently harsh to introduce defects on the nanofibers, though it is efficient at removing amorphous carbon and dispersing. In contrast, the tNF-u2 treated with 60w for 10 min has less defects. These results are also strongly supported by the TEM in the section of "morphology".

Taking into account a negligible shape change, we choose the pre-treatment with 60w and 10 min to maintain good uniformity in the F-C reaction.



4. FTIR spectra of nanofibers. (a) tNF, tNF-u1, and tNF-u2. (b) pNF, pNF-u1, and pNF-u2.

Fig. S1 FTIR spectra of nanofibers. (a) tNF, tNF-u1, and tNF-u2. (b) pNF, pNF-u1, and pNF-u2. (tNF and pNF are the raw materials, tNF-u1 and pNF-u1 were treated by sonication for 60 min at 100w, tNF-u2 and pNF-u2 were treated by sonication for 10 min at 60w)

5. FT-IR spectrum of tNF-(COOH)_{n2} heated at 120 $^{\circ}$ C for 2 h



Fig. S2 FT-IR spectrum of tNF-(COOH)_{n2} heated at 120 °C for 2 h.

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6. TGA analysis of nanofibers after sonication



Fig. S3 TGA analysis of nanofibers. (a) tNF, tNF-u1, and tNF-u2. (b) pNF, pNF-u1, and pNF-u2. (tNF-u1 and pNF-u1 sonicated with 100w for 60 min, tNF-u2 and pNF-u2 treated with 60w for 10 min)



7. Auger chemical composition analysis of nanofibers

Fig. S4 Auger chemical composition analysis of nanofibers. (a) tNF, tNF-u1, tNF-u2, tNF-(COOH)_{n2}, and tNF-SQ. (b) pNF, pNF-u1, pNF-u2, pNF-(COOH)_{n2}, and pNF-SQ.

8. Photoluminescence emission spectra



Fig. S5 Photoluminescence emission spectra of OASQ, tNF-SQ, pNF-SQ, tNF-A, and pNF-A in THF with an average of 50 mg/L. Alkali treatment: tNF-SQ and pNF-SQ were immersed in 1 mol/L sodium hydroxide solution overnight and washed with water and ethanol. They were then dried under vacuum at 75 °C for 72 h. The products were denoted as tNF-A and pNF-A, respectively. The emission wavelength for all PL measurements is 275 nm

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9. XRD patterns of nanofibers



Fig. S6 XRD patterns of nanofibers. (a) tNF, tNF-u1, tNF-u2, tNF-(COOH)_{n2}, and tNF-SQ. (b) pNF, pNF-u1, pNF-u2, pNF-(COOH)_{n2}, and pNF-SQ.

10. TEM images of nanofibers: (a) tNF, (b) pNF, (c) tNF-u1, (d) pNF-u1, (e) tNF-u2, (f) pNF-u2.



Fig. S7 TEM images of nanofibers: (a) tNF, (b) pNF, (c) tNF-u1, (d) pNF-u1, (e) tNF-u2, (f) pNF-u2. (tNF and pNF are the raw materials, tNF-u1 and pNF-u1 were treated by sonication for 60 min at 100w, tNF-u2 and pNF-u2 were treated by sonication for 10 min at 60w)

11. TEM images of nanofibers participated in the F-C reaction with various amount of oxalyl chloride



Fig. S8 TEM images of nanofibers participated in the F-C reaction with various amount of oxalyl chloride. (a) $tNF-(COOH)_{n0}$, (b) $pNF-(COOH)_{n0}$, (c) $tNF-(COOH)_{n2}$, and (d) $pNF-(COOH)_{n2}$.



12. Digital photographs of dispersion of nanofibers in THF

Fig. S9 Digital photographs of dispersion of nanofibers in THF. After sonication (left) and precipitation appears (right).



13. Nitrogen adsorption/desorption isotherms of nanofibers.

Fig. S10 Nitrogen adsorption/desorption isotherms of nanofibers. (a) Nitrogen adsorption/desorption isotherms of tNF, tNF-u2, and tNF-SQ. (b) Nitrogen adsorption/desorption isotherms of pNF, pNF-u2, and pNF-SQ. (tNF-u2 and pNF-u2: tNF and pNF were treated by sonication for 10 min at 60w, respectively)



14. TEM image of associated floating skims collected from nanofibers after sonication

Fig. S11 TEM image of associated floating skims collected from nanofibers after sonication. (a) tNF sonicated with 60w for 10 min, (a) pNF sonicated with 60w for 10 min, (c) tNF sonicated with 100w for 60 min, (d) pNF sonicated with 100w for 60 min

15. Raman spectra of tNF-u1, pNF-u1, tNF-u2 and pNF-u2.



Fig. S12 Raman spectra of tNF-u1, pNF-u1, tNF-u2 and pNF-u2.

16. Reference for the Supporting Information

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