

Construction and electronic properties of carbon nanotubes hybrids with conjugated cubic silsesquioxane

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1. The information about the chemicals and instruments

Hydrazine hydrate (80%), THF, DMF, DMSO, 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. 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. 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. Preparations of octa-aminophenylsilsesquioxane (OASQ)

Octa(nitrophenyl)silsesquioxane (ONSQ) was synthesized in our laboratory.¹ ONSQ (0.5g, 0.358mmol, $-\text{NO}_2$ 2.87 mmol), FeCl_3 (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 H_2O four times. The organic layer was dried over MgSO_4 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); ^{29}Si NMR (δ , ppm): -70.0 , -77.5 ; ^1H NMR ($\text{DMSO}-d_6$) (d, ppm): 7.8–6.2 (b, 2.0H), 5.2–3.7 (b, 1.0H).

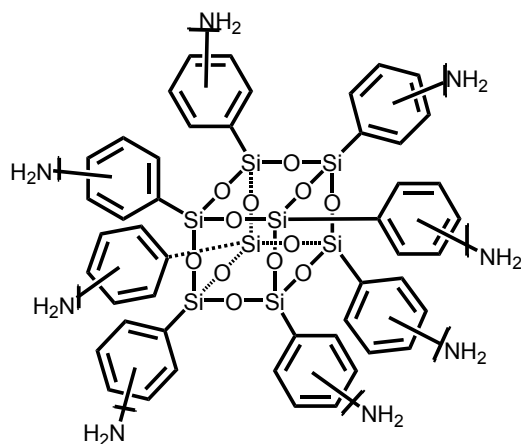


Figure S1 Octa-aminophenylsilsesquioxane

3. Preparations of octa(N-phenylbenzimine)silsesquioxane (PSBM)

Octa(*m*-formylphenyl)silsesquioxane (OFSQ) was synthesized in our laboratory according to literature methods.³ OFSQ (1.26g, 1mmol), aniline (1.49g, 16mmol) were charged into a three-necked 100 mL round-bottomed flask with a solvent mixture (DMSO 50 mL, ethanol 10 mL), using Zn (20 mg) as the catalyst. The reaction mixture was stirred at 85 °C for 4 h and then poured into 200 mL of H₂O. The obtained powder was collected by filtration, washing and dried. FTIR (KBr): 1619 (C=N), 1119 cm⁻¹ (Si-O-Si); ¹H NMR (DMSO-*d*₆) (d, ppm): 8.6 (1H, single, HC=N).

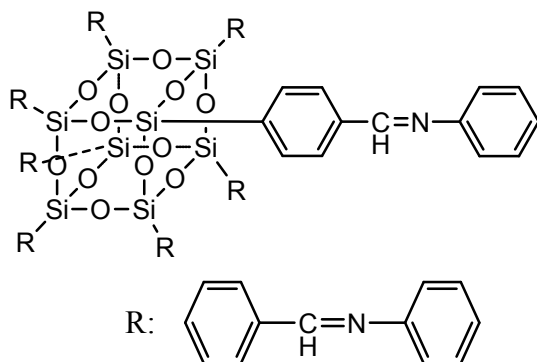


Figure S2 Schiff-base model compound with CSQ

4. Calculations of Schiff-base model compound

Calculations on the model molecules were performed using GAMESS program.⁴ Preoptimizations of the molecules were carried out using MM2 semiempirical quantum chemistry model.⁵ The resulting molecular configurations were used as the starting atomic coordinates for further optimization in the DFT frame. All calculations reported in this work were performed at the 6-31G(d)//6-31G(d) level, which was deemed to provide an acceptable compromise between the computational effort required and accuracy of calculated energies.

4. Characterization of functionalized SWNT

Thermogravimetric analysis (TGA) results of OASQ, SWNT, SWNT-COOH and SWNT-SQ are given in Fig. S3. The TGA curve of OASQ shows a rapid weight loss of 34 wt% in the range of 200–800 °C, due to the partially decomposed OASQ molecules. The weight loss of SWNT and SWNT-COOH from 30 °C to 200 °C is approximately 0.5% and 0.3 % probably attributed to little adsorbed moisture, and both two display excellent thermal stability in nitrogen. Indeed, the SWNT-COOH underwent an unobvious weight loss (6.7 wt %) at temperatures between 200 and 800 °C ascribed to the possible carboxyl groups attached to the surface. However, the weight loss of SWNT-SQ may consist of two parts: the weight loss OASQ molecules and carbonyl groups on the nanotubes. Combining the weight loss of free OASQ molecules and SWNT-COOH at the same temperature ranges, the weight percentage of OASQ (Table S1) in SWNT-SQ is estimated by an equation of the following type:

$$nSQ = (w - w_1) / (w_2 - w_1)$$

where w , w_1 , and w_2 are the weight loss from 200 to 800 °C of SWNT-SQ, SWNT-COOH, and OASQ, respectively.

The char yields at 800 °C are 96.25 %, 93.04 % and 74.80 % for SWNT, SWNT-COOH and SWNT-SQ respectively. The TGA results revealed that there was approximately a carboxyl group covalently attached to the nanotubes framework for 78 carbon sites corresponding to SWNT-COOH. The weight percentage of OASQ in SWNT-SQ is about 53.5 wt%. In other words, there is approximately an OASQ molecule covalently attached to the nanotubes framework for 87 carbon sites. After attaching to OASQ molecules, the thermal stability of the product declined slightly, and the OASQ moiety in the product is stable.

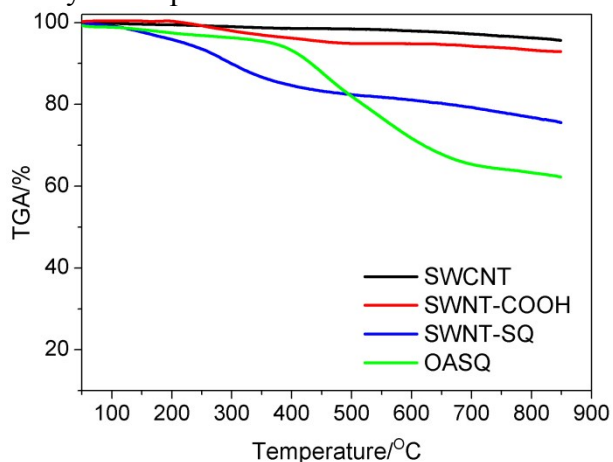


Figure S3 Thermogravimetric analysis (TGA) of SWNT, SWNT-COOH and SWNT-SQ.

Table S1 Thermogravimetric analysis (TGA) data of carbon nanotubes and functionalized carbon nanotubes

sample	200 °C weight loss %	550 °C weight loss %	800 °C weight loss %	Degree of functionalization ^a
SWNT	0.53	1.43	3.75	416
SWNT-COOH	0.31	5.13	6.96	78
OASQ	2.53	23.26	36.68	N/A
SWNT-SQ	3.83	22.62	25.20	87

^a The degree of functionalization: the ratio of number of carbon atoms to number of grafted groups when carboxylic groups or SQ molecules attached to the nanofibers surface.

5. Electrochemical Analysis



Figure S4 Photographs of flexible nanotubes films and cross-sectional view of SWNT-SQ.

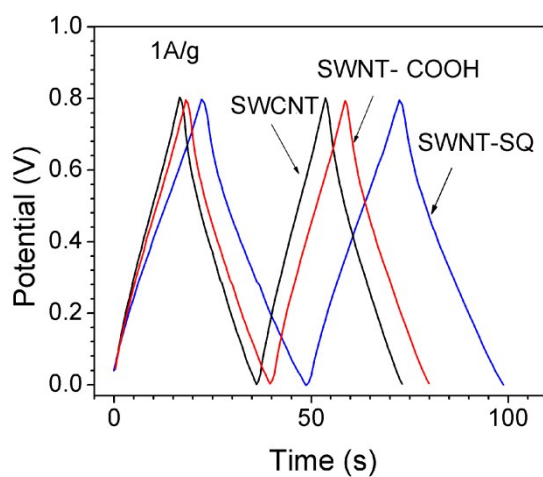


Figure S5 Galvanostatic charge-discharge curves for SWNT, SWNT-COOH, and SWNT-SQ electrodes. The charge-discharge current density is 1.0 A/g in 0.5 M K_2SO_4

6. Reference for the Supplementary Information

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