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Synthesis of Ultrathin Mesoporous Carbon through Bergman Cyclization of Enediyne Self-Assembled Monolayers in SBA-15

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In this work, a bottom-up synthesis of ultrathin mesoporous carbon was developed through Bergman cyclization of enediyne containing compounds immobilized inside of SBA-15 nanochannels and followed by pyrolysis. Raman spectroscopy confirmed the occurrence of thermal Bergman cyclization inside the channels. Further heating under elevated temperature produced nanotube arrays in good yield. TEM images revealed the formation of interconnected tubular carbon due to the microtunnels of template. Raman spectra showed moderate degree of graphitization. Formation of enediyne SAMs on a template followed by the processing sequence developed in this work is promising to construct carbon materials with various nanoscopic morphology, such as carbon nanotube, graphene, and giant fullerene.

Introduction

Carbon, as one of the most important substances, possesses a broad range of properties due to the existence of different allotropes as well as various microstructures. Seminal work by Smalley¹ et al. on carbon buckyball, Iijima² on carbon nanotubes and Geim et al.³ on graphene had initiated tremendous research efforts on many preparation methods of these nanoscopic materials, including arc discharge, chemical vapor deposition (CVD), laser evaporation, thermal decomposition, ion beam irradiation, and nanocasting.^{4–16} The applications of these materials had also

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been widely demonstrated in catalyst supports, gas storage, nanofiltration, fuel cell, and electrode materials. $^{16-22}$

Morphology control is generally very critical in the synthesis of nanomaterials since the properties of nanomaterials are highly structural dependent. Tremendous work had been focused on synthesizing nanomaterials with various shapes, including rods, tubes, pipes, prisms, cubes, spheres, capsules, and sheets. Among all these efforts, templated synthesis $^{15,23-30}$ belongs to one of the most important approaches to achieve nanomaterials with unique shapes that could not be easily obtained through other methods. Elegant work on controlled synthesis of mesoporous silica³¹⁻³⁴ had provided a variety of hard templates, which facilitate the construction of different types of nanomaterials. Ryoo et al.³⁵ accomplished the synthesis of ordered carbon nanopipes inside rigid mesoporous silica templates by filling the voids with furfuryl alcohol through incipient-wetness technique followed by pyrolysis under elevated temperature. The obtained carbon nanopipes were proven to be good supports for Platinum nanoparticles in electrocatalytic reduction of oxygen. Following this strategy, a number of researches had been conducted either by switching carbon precursors from furfuryl alcohol to phenol resin,

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polyacrylonitrile, acenaphthene, etc. or by using other templates, such as anodic aluminum oxide (AAO) or metal-organic frameworks (MOF).^{36–50} However, pyrolysis reactions are chemically complicated and difficult to control, and void-filling technique is not suitable for making replica of flat or external surface of templates. Formation of self-assembled monolayers (SAMs) of multifunctional precursors on template followed by cross-linking reaction had been established in the synthesis of poly-(arylenediacetylene) monolayers of different shapes.⁵¹ Biphenyl thiol SAMs on gold surface irradiated with electron beam followed by high temperature pyrolysis has recently be proven to produce ~ 1 nm thick conducting aromatic nanosheets.⁵² Single layer graphene sheets were prepared using oxidative cross-linked polypyrrole as carbon source through a confined self-assembled approach.⁵³ We deduce that with rational designed monomers, infinite sp² carbon network could be synthesized in "bottom-up" manner under suitable polymerization conditions, which will facilitate construction of graphitic monolayers with various morphologies. Herein, we wish to report our work on synthesizing ultrathin mesoporous carbon through processing Bergman cyclization of enediyne SAMs on internal surface of mesoporous silica SBA-15.

Bergman cyclization is the intramolecular cyclization of enediyne compounds first studied by Bergman et al.⁵⁴ It was later found that many naturally occurring enediyne-containing compounds exhibited strong antibiotic activities through *in situ* triggered Bergman cyclization.⁵⁵ Extensive research had been focused on elucidation of the mechanism of Bergman cyclization

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and synthesizing biosimilar compounds as potential anticancer agents.^{56–60} Bergman cyclization had also been used in surface functionalization of multilayered carbon nano-onion and C_{60} ,^{61,62} initiating free radical polymerization,⁶³ and formation of glassy carbon.^{64–66} It is well established that with properly designed enediyne precursors, extensive polyarene network can be obtained through Bergman cyclization, which is essential for formation of sp² carbon monolayers inside the channels of SBA-15 in this work.

Experimental Section

Materials. Tetrahydrofuran (THF) and triethylamine (Et₃N) were distilled over sodium or calcium hydride under nitrogen prior to use. Other reagents used in the reactions were analytically pure and used as received. All of the reactions and manipulations were carried out under a nitrogen atmosphere and using Schlenk techniques. 4-(2-(trimethylsilyl)ethynyl)benzaldehyde and 4-ethynylbenzaldehyde (1) were synthesized according to literature procedure with minor modification,⁶⁷ detailed information could also be found in Supporting Information. All chromatographic purifications were performed on silica-gel (200–300 mesh) using the indicated solvent systems.

Characterization. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in chloroform-d (CDCl₃) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/54 mm). Onset and peak temperature of the model compound were studied with Differential Scanning Calorimetry (DSC) using a Pyris Diamond thermal analysis workstation equipped with a model 822e DSC module under a constant nitrogen flow. FT-IR spectroscopy measurements were performed from KBr pellets on a Nicolet Magna 5700 FTIR spectrometer. Mass spectra were obtained with a Micromass LCTTM mass spectrometer using EI method. X-ray diffraction (XRD) patterns were conducted on a Bruker D8 ADVANCE (Karlsruhe, Germany) X-ray diffractometer (Cu Ka radiation generated at 40 kV and 40 mA). The sample for TEM dispersed in anhydrous isopropanol was deposited on a grid of holey carbon film and transferred to a JEM-2100F high resolution transmission electron microscope operating at 200 kV. Raman measurements were performed on an inVia+Reflex Raman spectrometer (Renishaw, 514 nm). Nitrogen adsorption/desorption isotherms were measured at 77 K with an adsorption apparatus (Micromeritics, ASAP 2010 V5.02). The surface area of the samples was determined from the Brunauer-Emmett-Teller (BET) equation and pore volume, from the adsorption branches of the isotherms with use of the Barrett–Joyner–Halanda (BJH) method.

Synthesis. 4-(2-(2-Bromophenyl)ethynyl)benzaldehyde (2). A degassed solution of 1 (4.43 g, 34 mmol), 1-bromo-2-iodobenzene (10.47 g, 37 mmol), Pd(PPh₃)₂Cl₂ (0.71 g, 1.02 mmol), and CuI (0.19 g, 1.02 mmol) in 35 mL of anhydrous Et₃N was heated at 60 °C overnight under a nitrogen atmosphere. After cooling, the resulting solution was concentrated and then partitioned with saturated aqueous NaCl, 1 M HCl, and ethyl acetate. The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum and the residue was

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purified by silica gel chromatography with petroleum ether/ ethyl acetate (20/1) as eluent to give 7.37 g of product as yellow crystal. Yield: 76%. ¹H NMR (CDCl₃, ppm): 10.03 (s, -HC=O, 1H), 7.61–7.79 (m, O = CH-Ph-H, 4H), 7.13–7.55 (m, Br– Ph–H, 4H). ¹³C NMR (CDCl₃, ppm): 190.1, 134.4, 132.2, 131.3, 130.9, 128.8, 128.3, 127.8, 125.9, 124.6, 123.4, 91.5, 90.6. MS: m/zcalcd for C₁₅H₉BrO, 284.0; found, 284.0.

4-(2-(2-(2-(Trimethylsilyl)ethynyl)phenyl)ethynyl)benzaldehyde (3). A degassed solution of 2 (7.37 g, 26 mmol), Pd-(PPh₃)₂Cl₂ (0.54 g, 0.78 mmol), and CuI (0.15 g, 0.78 mmol) in 70 mL of anhydrous Et₃N was treated with trimethylsilylacetylene (TMSA) (26.3 mL, 182 mmol). The mixture was heated in the seal tube at 80 °C for 3 days. After cooling, the resulting solution was concentrated and then partitioned with saturated aqueous NaCl and ethyl acetate. The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum and the residue was purified by silica chromatography with hexane/ethyl acetate (35/1) as eluent to give 5.98 g of yellow oily liquid. Yield: 73%. ¹H NMR (CDCl₃, ppm): 10.02 (s, -HC=O, 1H), 7.69–7.89 (m, O = CH - Ph - H, 4H), 7.30–7.55 (m, $(CH_3)_3$ – Si-C=C-Ph-H, 4H), 0.27 (s, $-Si-(CH_3)_3$, 9H). ¹³C NMR (CDCl₃, ppm): 191.1, 135.2, 132.3, 132.1, 131.9, 131.6, 129.3, 129.2, 128.3, 128.0, 125.7, 124.9, 102.9, 98.8, 92.0, 91.9, 0.28. MS: m/z calcd for C₂₀H₁₈OSi, 302.1; found, 302.1.

4-(2-(2-*Ethynylphenyl*)*ethynyl*)*benzaldehyde* (4). A degassed solution of **3** (5.98 g, 19 mmol), tetrabutylammonium fluoride (TBAF) (9.94 g, 38 mmol) and *p*-toluenesulfonic acid (PTSA) (3.27 g, 19 mmol) in 60 mL of anhydrous THF was stirred under a nitrogen atmosphere for 10 min at room temperature. The solvent was removed under vacuum and the residue was purified by silica gel chromatography with petroleum ether/ethyl acetate (7/1) as eluent to give 4.33 g of yellow oily liquid. Yield: 99%. ¹H NMR (CDCl₃, ppm): 10.00 (s, -HC=O, 1H), 7.68–7.86 (m, O=CH-Ph-H, 4H), 7.32–7.56 (m, HC=C-Ph-H, 4H), 3.41 (s, -C=CH, 1H). ¹³C NMR (CDCl₃, ppm): 191.7, 135.8, 133.0, 132.5, 132.2, 129.8, 129.6, 128.9, 125.7, 125.2, 92.7, 92.0, 82.2, 81.8. MS: *m/z* calcd for C₁₇H₁₀O, 230.1; found, 230.1.

N-(4-(2-(2-Ethynylphenyl)ethynyl)benzylidene)-3-(triethoxysilyl)propan-1-amine (5). A degassed solution of 4 (4.33 g, 19 mmol), 3-aminopropyltriethoxysilane (APTES) (3.98 g, 18 mmol), and 1 g of MgSO₄ in 40 mL of anhydrous ethanol was stirred at room temperature overnight under a nitrogen atmosphere. The resulting solution was filtrated and the solvent was removed under vacuum to give 8.07 g of yellow oily liquid. Yield: 98%. ¹H NMR (CDCl₃, ppm): 8.13 (s, -HC=N, 1H), 7.58-7.72 (m, -N=CH-Ph−*H*, 4H), 7.29−7.55 (m, HC≡C−Ph−*H*, 4H), 3.79−3.85 (m, (CH₃-CH₂-O)₃-Si-, 6H), 3.61-3.64 (t, -CH₂-N=CH-, 2H), 3.38 (s, $-C \equiv CH$, 1H), 1.81–1.85 (t, $-CH_2 - CH_2 - N = CH_-$, 2H), 1.18-1.24 (m, $(CH_3-CH_2-O)_3-Si-$, 9H), 0.65-0.70 (t, -CH₂-Si-(OCH₂CH₃)₃, 2H). ¹³C NMR (CDCl₃, ppm): 160.4, 136.2, 132.6, 132.0, 131.9, 128.6, 128.1, 128.0, 126.1, 125.2, 124.7, 93.3, 89.6, 82.1, 81.3, 64.4, 58.4, 24.3, 18.3, 8.1. MS: m/z calcd for C₂₆H₃₁NO₃Si, 433.2; found, 433.3.

Synthesis of SBA-15. Mesoporous silica SBA-15 was synthesized according to published procedures.^{31,32,68} In a typical synthesis, 5 g of triblock copolymer surfactant $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Sigma-Aldrich) was dissolved in 159.5 g of distilled water and 26.5 mL of 12 M HCl with stirring, followed by addition of 10.4 g of tetraethoxysilane (TEOS) at 40 °C. This gel was continuously stirred for 20 h and then hydrothermally treated at 100 °C for 24 h. After crystallization, the solid product was filtered, washed with distilled water, and dried in air at 40 °C. The material was calcinated in air at 550 °C for 5 h to remove the surfactant template and obtain a white powder (as-synthesized SBA-15). As-synthesized SBA-15 was dispersed in piranha solution (H₂SO₄:H₂O₂=7:3, volume ratio) [*Caution! Piraha solution is* *highly corrosive and toxic*] with 30 min sonication, and heated at 90 °C for 24 h. After activation, the resulting mixture was centrifuged (9500 rpm, 15 min) and rinsed with deionized water to neutrality and then washed with anhydrous ethanol repeatedly to obtain a white powder (SBA-15-Cal/P).

Immobilization. Imine **5** (1.06 g) and activated SBA-15 (1.18 g) were mixed in 50 mL Schlenk flask, and then 20 mL of anhydrous ethanol was added under a nitrogen atmosphere. After stirred for 40 h at 85 °C, the resulting solution was centrifuged (9500 rpm, 15 min) and rinsed with anhydrous ethanol repeatedly to obtain a pale yellow powder (EDY-SBA-15-Cal/P, note: EDY represents enediyne). Weight percentages of EDY immobilized on silica were between 35% and 40%.

Bergman Cyclization. All the Bergman cyclization (BC) reactions were performed under vacuum in a sealed glass tube with EDY-SBA-15-Cal/P inside and diphenyl ether outside as reflux bath (259 °C) for 8 h to obtain a brown powder (BC-EDY-SBA-15-Cal/P).

Pyrolysis. All the pyrolysis reactions were performed in a tube furnace with a continuous nitrogen flow. BC-EDY-SBA-15-Cal/ P was heated in a furnace while the temperature was increased to 750 °C at a rate of 2.0 °C min⁻¹, and then maintained for 1 h to obtain a black powder (CNT-SBA-15-Cal/P). After pyrolysis, the weight-loss ratio of sample was approximately 25%.

Removal of Template. Silicon etching was performed in a PTFE griffin beaker at ambient temperature. CNT-SBA-15-Cal/ P was treated with 40% HF and stirred vigorously at ambient temperature overnight to remove the silicon template.

Results and Discussion

Synthesis of Enediyne-Containing Imine (5). Enediyne 4 was synthesized by three consecutive Sonogashira coupling reactions in high yields. 4-ethynylbenzaldehyde (1) was first synthesized through a known procedure (see Supporting Information).⁶⁷ Reaction of 1 with commercial available o-bromoiodobenzene afforded 2 in good yield. In this reaction, iodine was selectively substituted while bromine was intact according to NMR and MS analysis. Subsequent installation of trimethylsilylacetylene (TMSA) took place in a sealed tube under elevated temperature, and then the trimethylsilyl protection group was completely removed using a solution of TBAF and PTSA in THF. TBAF is typically used as a selective and mild deprotection reagent for the trimethylsilyl (TMS) group. However, we found that lots of unidentified byproduct formed when using solely TBAF to remove TMS group of 3. This phenomenon was speculated as due to the strong basicity of fluorine anions in TBAF solution. To solve this problem, a half equivalent of PTSA was added to the reaction mixture to neutralize fluorine anions into bifluoride. With this combo deprotection reagent, the reaction took place cleanly to form 4 in quantitative yield. The final imine product 5 was successfully formed by reacting 4 with APTES in anhydrous ethanol. A slight excess of enediyne 4 was used in this reaction to avoid incorporation of free APTES (enediyne void in SAMs) on templates in the subsequent immobilization step (Scheme 1).

Formation of Carbon Monolayers. With this enediyne containing imine (**5**) in hand, SAMs formation could be processed straightforwardly on various substrates. In this work, we chose internal surface of SBA-15 as the substrate to construct tubular carbon monolayers. Pretreated SBA-15 powder was added to a reflux solution of **5** in anhydrous ethanol, the immobilization was conducted under nitrogen atmosphere for 40 h. After thoroughly rinsed with anhydrous ethanol, a pale yellow powder was obtained. The enediyne grafted SBA-15 was then heated to 260 °C under vacuum. Differential calorimetry scan (DSC) analysis showed that Bergman cyclization of **4** takes place rapidly at over

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Scheme 1. Synthesis of Enediyne Containing Imine^a



^{*a*} Key: (a) 4-ethynylbenzaldehyde (1), Pd(PPh₃)₂Cl₂, CuI, Et₃N, 60°C, 76%. (b) TMSA, Pd(PPh₃)₂Cl₂, CuI, Et₃N, 80°C, 73%. (c) TBAF, PTSA, THF, 99%. (d) APTES, EtOH, RT, 98%.



Figure 1. Schematic illustration of formation of 2D carbon network inside SBA-15 channels.

200 °C (see Supporting Information). After thermal Bergman cyclization, the powder turned to light brown. Raman analysis confirmed the reaction was complete according to the disappearance of the alkyne moieties (\sim 2220 cm⁻¹). The powder was heated in a tube furnace at 750 °C for 1 h to eliminate any volatile components. The black powder obtained was treated with aqueous HF solution to give the carbonous material. This powder was heated under vacuum at 900 °C to further fix the carbon network.

As shown in Figure 1, the formation of densely packed SAMs is the fundamental prerequisite in construction of an infinite sp² carbon network. The choice of template is thus highly important. SBA-15 prepared from conventional methods, either by calcination or solvent extraction, did not meet with this criterion. Irregular flakes or giant semitransparent carbonous materials were obtained after removal of templates due to lost of some surface hydroxy groups during calcination or channel collapse during solvent extraction (see Supporting Information). Zhao et al.⁶⁹ reported that treating as-synthesized SBA-15 through a high pressure microwave digestion process in the presence of concentrated nitric acid and hydrogen peroxide, most surface



Figure 2. TEM images viewed along [110] (A) and [001] (B) directions, SAED (inset) pattern of tubular carbon monolayers, and EDX spectrum (C) of tubular carbon monolayers after removal of template.

Si-OH were maintained for further functionalization. To avoid using this relative harsh condition with operating highly corrosive acid under high pressure and high temperature, we chose an alternative strategy to activate the silica surface by treating the calcinated SBA-15 with Piranha solution. IR analysis clearly showed intense Si-OH bending band at around 960 cm⁻¹. After immobilization of **5**, this band was completely disappeared (see Supporting Information), indicative of formation of densely packed enediyne SAMs. With this activated SBA-15 as template, well-defined tubular carbon monolayers were obtained as shown in TEM images (Figure 2).

The pore structure of SBA-15 is revealed as a complex combination of meso-channels and significant amount of microtunnels.⁷⁰ Most of replica method for preparation of other mesoscopic materials relied on these microtunnels to hold the

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Figure 3. Nitrogen adsorption isotherm of tubular carbon monolayers.

nanowires together after removal of silica template. From TEM images, it is obvious that nanotubes prepared through this method were holding together through irregular nanorods. Fast Fourier transform (FFT) diffractograms also showed maintenance of mesophase (see Supporting Information). Energy dispersive X-ray spectroscopy (EDX) measurement showed no detectable silicon signal (Figure 2), which confirmed that these tubular carbon monolayers were interconnected with carbonous matter originated from replica of microtunnels of SBA-15 template. The carbon bridges are relatively weak, after sonication in isopropanol for prolonged time (TEM sampling), some discrete carbon nanotube arrays or single nanotubes can be found in TEM (see Supporting Information). Select area electron diffraction (SAED) of carbon networks showed two well separated rings with d spacings of 0.217 and 0.126 nm, which could be interpreted as to correspond to the major indices [100] (0.123 nm) and [110] (0.213 nm) of graphite nanostructure. The fact that the [100] ring appear to be more intense than the [110] ring further reflects the single-layer nature of the tubular arrays.⁵³ To prepare independent carbon nanotubes, micropore-less template like MCM-41 or SBA-15 prepared in the presence of concentrated inorganic salts⁷⁰ could be used. This work will be presented in the future.

Nitrogen adsorption data (Figure 3 and Supporting Information) showed that tubular carbon monolayers exhibited high surface areas (around 1500 m²/g) and large pore volumes (above 1.0 cm³/g, BJH) with significant amount of micropores (~ 0.2 cm³/g, BJH). The mesopores of all samples have uniform size distribution centered at 3.8 nm, which is comparable to the mean diameter of carbon channels measured from TEM images. The XRD of SBA-15 template showed three well-resolved peaks revealing a highly ordered hexagonal (*p6mm*) pore structure similar to reported data.^{31,32} After removal of silica, tubular carbon monolayers showed much less intense diffraction peaks, indicative of less ordered structures.

Raman spectra (Figure 4) showed two broad peaks centered at 1350 and 1590 cm⁻¹ corresponding to so-called D, G bands. The G band is related to the in-plane E_{2g} vibration mode of graphite sp²-bonded carbon atoms in a 2D hexagonal lattice, while D-peak is due to the breathing mode of the aromatic rings, which are



Figure 4. Raman spectra of tubular carbon monolayers.

active in graphitic materials exhibiting structure defects.⁷¹ After annealing at 900 °C, the G-peak shifted to higher wavenumber, reaching 1598 cm⁻¹ (Figure 3). The intensity ratios of I_D/I_G of carbon nanotubes are around 0.8–0.9 for these nanotubes, which are comparable to other graphitic nanostructures prepared through catalytic polymerization followed by pyrolysis,^{39,52,53} indicative of moderate graphitization degrees in these samples.

Control experiments were conducted using simple aromatic imines synthesized from APTES with benzaldehyde or 2-naph-thaldehyde. These imines were first immobilized onto activated SBA-15 and then pyrolyzed under continuous nitrogen flow. All organic components were completely burned off when the samples were heated to 750 °C. These results unambiguously confirmed the necessity of Bergman cyclization in constructing infinite carbon network and final tubular carbon monolayers in this work.

Conclusion. We have developed a universal and simple method to synthesize ultrathin mesoporous carbon inside nano channels of mesoporous silica. The integrity of tubular shape of silica was fully maintained after etching off the template. The facial synthesis and structural variability of enediyne precursors allow bottom-up construction of a family of graphitic monolayers on various substrates, which can further be extended to the synthesis of giant fullerene and mass production of graphene. These works are currently underway in our lab.

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Supporting Information Available: Text giving detailed experimental procedures for starting materials, figures showing NMR spectra, DSC curve, TGA analysis, IR spectra, Raman spectrum, XRD patterns, and TEM images, and a table of BET data. This material is available free of charge via the Internet at http://pubs.acs.org

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