SPECIAL TOPIC — The third carbon: Carbyne with one-dimensional sp-carbon

Large-scale synthesis of polyynes with commercial laser marking technology

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The space-confined synthesis method has been an efficient way for the preparation of linear carbon chains. However, the large-scale preparation of linear carbon chains still faces many challenges due to the lack of methods for the large-scale synthesis of precursors, such as short carbon chains (polyynes), and regulation technology for the transport of reactants in one-dimensional space. Here, we report a facile method for the rapid preparation of polyynes in large quantities using a commercial laser marking machine. Spectroscopic characterizations show that a large number of polyynes, such as C_8H_2, $C_{10}H_2$, $C_{12}H_2$, and $C_{14}H_2$, can be produced by ablating the graphite plate immersed in the organic liquid using a laser marking machine. The results of *in situ* Raman spectroscopy investigation of $C_{2n}H_2$-filled single-walled carbon nanotubes further confirm that a variety of polyyne molecules are synthesized. Meanwhile, *in situ* Raman spectroscopy also shows that the local heating treatment can accelerate the filling process of $C_{2n}H_2$ into one-dimensional channels. This work provides new insights into the study of linear carbon chains and space-confined synthesis methods.

Keywords: polyynes, carbon chains, single-walled carbon nanotubes

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1. Introduction

Carbyne, long linear carbon chain (LLCC), as a pure sp-hybridized carbon material,[1,2] has been studied for decades.[3–5] However, the synthesis of carbyne with infinite-length LLCCs still faces many challenges such as the instability in the ambient, the crosslink reaction between LLCCs, and the high activity from nearly naked carbon atoms.[6] Therefore, the space-confined nanoreactors,[3,7–12] especially some one-dimensional channels like carbon nanotubes (CNTs), have been used as nanoshells to protect and prepare LLCCs. At the same time, short linear carbon chains (polyyne), such as $C_{2n}H_2$ ($n = 1, 2, 3, \ldots$), composed of alternating single and triple bonds through end-capped bonding with hydrogen, have been considered as the most important precursors for the synthesis of LLCCs.[8,12]

Now many reports have successfully synthesized the confined LLCCs in CNTs.[3,7,8,10–12] However, there are still many challenges in this field. One problem is the lack of a simple and efficient technology to prepare polyynes. Although several strategies have reported the synthesis of $C_{2n}H_2$, such as laser-ablation,[13–15] arc-discharge method,[16–18] and chemical synthesis method,[19–21] they still need complex devices and show low-efficiency in the preparation of polyynes. Additionally, an efficient method to regulate the transport of precursors in one-dimensional channels is a key for the synthesis of confined LLCCs. However, the existing methods are powerless to regulate the molecules in confined space.[8,12] Therefore, a facile, low-cost, and efficient approach to prepare $C_{2n}H_2$ and research on the filling process of $C_{2n}H_2$ into CNTs are urgently needed.

In this paper, we report a simple, low-cost technology for the preparation of $C_{2n}H_2$ on a large scale by a civilian laser marking machine. UV absorption spectroscopy and XPS spectroscopy reveal that polyynes, such as C_8H_2, $C_{10}H_2$, $C_{12}H_2$, and $C_{14}H_2$ have been prepared by a laser marking machine. At the same time, we observe the filling process of single-walled carbon nanotubes (SWCNTs) with $C_{2n}H_2$ by *in-situ* Raman spectroscopy, further confirming that polyynes have been prepared and successfully filled into the nanoreactor.

2. Experimental details

2.1. Preparation of C_2H_{2n}

The polyynes were prepared with a laser marking machine. The laser marking machine is equipped with a CO_2 laser. The wavelength is 1064 nm, the power is 40 W, and the diameter of the laser spot is about 10 μm. A typical preparation process is to scan a 15 mm×15 mm area on the graphite plate in *n*-hexane solution with a scanning speed of 100 mm/s for 1 hour. During the process, the *n*-hexane solution should be kept at a low temperature to avoid excessive evaporation. Finally, a highly concentrated polyyne solution was obtained by filtering and concentrating process.

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2.2. Preparation of SWCNT film and paper

The SWCNTs used in the experiments were prepared by the edips method with an average diameter of 1.3 nm.[22] After purification,[23] 2-mg SWCNTs, and 200-mg sodium dodecyl sulfate (SDS) (99%, Alfa Aesar) were added to 100 ml of deionized water. An ultrasonic homogenizer equipped with a 0.5-inch (1 inch = 2.54 cm) flat tip at 400 W worked for about 60 min. The dispersion was centrifuged at 1000 rpm for 5 min to remove undispersed SWCNTs, and 80% of the supernatant was stored at a low temperature (4 °C) for the preparation of SWCNTs films.

SWCNT thin films were prepared by the vacuum filtration method.[24] Firstly, the SWCNT dispersion was filtered through a nitrocellulose membrane (GSWP02500, Millipore), and then pasted on a 30×30 quartz sheet and dried. The filter membrane was removed by washing with ethyl acetate. Finally, the SWCNT films were treated in the air at 475 °C for 60 min.

2.3. *In situ* filling SWCNTs with polyynes

During the Raman test, 10 μl of polyyne solution was dropped on the SWCNT film. After 1 min, the Raman spectrum of the SWCNT film was recorded at the same point. This process was repeated for many times, and needed to keep the laser of the Raman spectrometer irradiating during the whole process.

2.4. Characterization

The polyynes and SWCNTs filled with polyynes were evaluated by Raman spectrometers (Renishaw InVia-plus and Horiba LabRAM HR evolution) equipped with 532-nm excitation lasers and UV-vis-NIR spectroscopy (Lambda750, Perkinelmer). The SWCNTs were evaluated by a high-resolution transmission electron microscope (HRTEM, Tecnai G2 20 200 kV) and scanning electron microscope (SEM, Hitachi SU8220). The chemical states of SWCNTs filled with polyynes and ablated graphite were analyzed with an x-ray photoelectron spectrometer (XPS, Thermo Scientific K-ALPHA).

3. Results and discussion

Figure 1(a) shows the photograph of the preparative device of $C_{2n}H_2$ in *n*-hexane solution with a laser marking machine. The energy of the laser focused on the surface of the graphite plate and then ablated the graphite. At the same time, new substances were produced in the ablation process. Figure 1(b) presents the ultraviolet optical absorption spectrum of the solution ablated by a laser marking machine. In the spectrum, four strong absorption peaks at 227, 252, 276, and 297 nm, marked in Fig. 1(b), correspond to C_8H_2, $C_{10}H_2$, $C_{12}H_2$, and $C_{14}H_2$, respectively, according to previous reports.[14,17,18] No other absorption peak is detected in the *n*-hexane solution. These results suggest that the $C_{2n}H_2$ molecules can be prepared by a laser marking machine ablating the graphite plate.

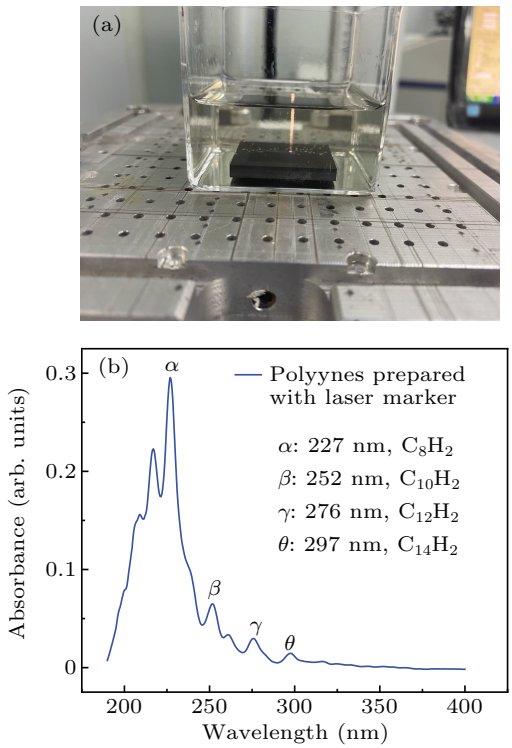


Fig. 1. $C_{2n}H_2$ prepared by laser marking machine. (a) Photograph of the preparative device for $C_{2n}H_2$, (b) ultraviolet optical absorption spectrum of $C_{2n}H_2$.

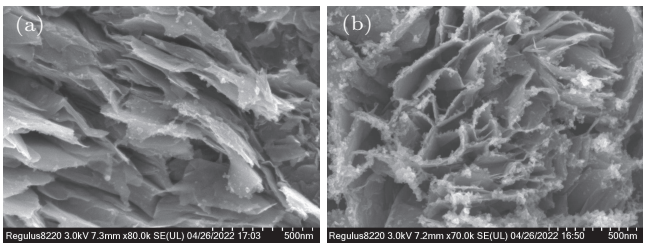


Fig. 2. SEM images of graphite plate before and after ablation. (a) SEM image of raw graphite plate, (b) SEM image of graphite plate after ablation.

After laser ablation, the color of the graphite sheet surface in the middle area becomes darker and the reflection is weakened, compared to the edge of the graphite plate without ablation, as shown in Fig. S1 in the supporting information. As shown in Fig. 2(a), before ablation, the surface of the graphite plate exhibits a flake structure, and the edge of the flake is clean. After laser ablation in Fig. 2(b), the surface of the graphite plate still maintains the initial morphology, but many non-uniform nanoparticles appear and adsorb on the edge and surface of the sheets. Relative to the raw graphite plate, the C 1s peak in x-ray photoelectron spectroscopy (XPS)

of the graphite plate ablated by laser marking machine has a slight redshift (about 0.1 eV) in Fig. S2 in the supporting information. This shift towards the low binding energy means the presence of the carbon–carbon triple bond (sp-hybridization). These results indicate that some graphite sheets have been ablated by the laser marking machine, and some carbon materials containing sp-hybridized carbon have formed on the surface of the graphite.

Figure 3(a) shows the SEM image of SWCNT film. The bundles of SWCNTs are uniformly distributed, and the SWCNT bundles show high quality without other impurities, which indicates that the filter membrane has been fully dissolved and removed during the preparation of the SWCNT film. As shown in Fig. 3(b), the TEM image further confirms the maintenance of high-quality SWCNTs with good structural integrity during the film preparation process. These results show that the surface structure of SWCNTs is not destroyed in the film preparation process, which is extremely beneficial for the filling step of $C_{2n}H_2$.

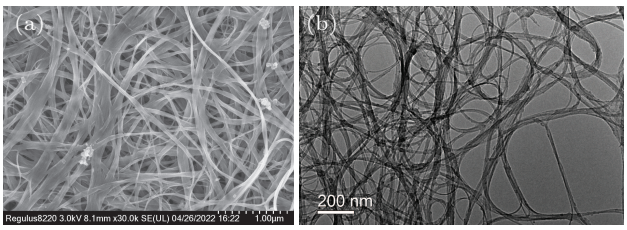


Fig. 3. SEM image of SWCNT film (a) and TEM image of SWCNTs (b).

To further investigate $C_{2n}H_2$, the $C_{2n}H_2$ *n*-hexane solution was dropped on the SWCNT film at room temperature, as shown in Fig. 4(a). Raman spectrometer was used to record the characteristic vibrations of the carbon–carbon triple bond (sp-hybridization) during the continuous dripping process. In addition to the original SWCNTs, in all Raman spectra from Fig. 4(b), an obvious range at about 1800 cm^{-1}–2200 cm^{-1}, corresponding to the stretching vibration of triple bonds in LCCs, which is assigned as C-mode,[25–27] is observed. Moreover, with the gradual drop of $C_{2n}H_2$ solution, the intensity of C-mode at 2068.2 cm^{-1} increases. To confirm the stability of $C_{2n}H_2$ in the SWCNTs, after the SWCNT film was dropped by the $C_{2n}H_2$ *n*-hexane solution for 50 times, the SWCNTs were treated at 300 °C in the air for 2 hours. We can see the intensity of C-mode for the SWCNTs film filled with $C_{2n}H_2$ shows no obvious change. In Fig. S3, the relative intensity of C-mode is 0.08 compared to that of G-peak, demonstrating the *in-situ* Raman signal in the filling process mainly comes from the internal $C_{2n}H_2$. These results indicate that a large amount of $C_{2n}H_2$ has been successfully filled into the SWCNTs, and with the increase of the amount of $C_{2n}H_2$ in the SWCNTs, the Raman intensity of C-mode gradually becomes stronger. Moreover, the most important is that the center position of the C-mode undergoes a significant redshift during the filling process. In Fig. 4(b), the center of the C-mode is located at 2068.2 cm^{-1} in the first filling process. However, as the number of drops increases, the center of C-mode gradually red-shifts, and finally stabilizes at 2056.7 cm^{-1}, indicating the frequency of the stretching vibration of $C_{2n}H_2$ within the confined space decreases due to the confinement effect.

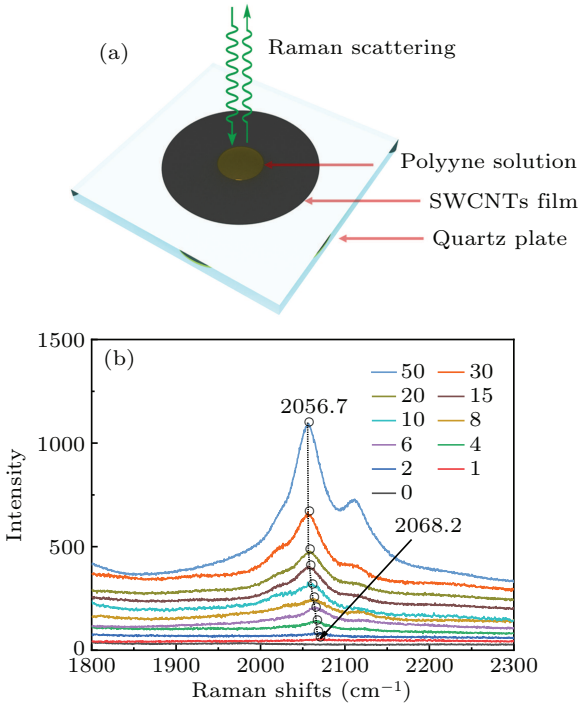


Fig. 4. *In situ* filling of SWCNTs with $C_{2n}H_2$. (a) Schematic diagram of filling SWCNTs with $C_{2n}H_2$. (b) Raman spectra of $C_{2n}H_2$ filled into SWCNTs.

The x-ray photoelectron spectroscopy (XPS) measurements were performed to evaluate the surface chemical composition of the initial SWCNT and $C_{2n}H_2$-filled SWCNT film. The $C_{2n}H_2$-filled SWCNT film has been treated at a high temperature to remove the $C_{2n}H_2$ on the surface of SWCNT film. In Fig. 5, high-resolution C 1s spectra of SWCNT and $C_{2n}H_2$-filled SWCNT film were shown. To compare the chemical composition of SWCNT films before and after being filled with $C_{2n}H_2$, we firstly corrected the two curves according to the binding energy position of the carbon–carbon single bond (284.8 eV). In the C 1s spectrum of $C_{2n}H_2$-filled SWCNT film, four peaks centered at 283.9, 284.8, 285.7, and 286.6 eV can be deconvoluted, which correspond to the sp^2 carbon, sp^3 carbon, C=O bond, and C–O bond, respectively. Relative to SWCNTs, the existence of C–O and C=O peaks for $C_{2n}H_2$-filled SWCNTs indicates that the filling process does not affect the surface functional groups of SWCNTs. The reduction of the sp^3 carbon content may be due to the heat treatment after

filling, resulting in a decrease in surface adsorption of carbon. Compared with that of the original SWCNTs, the peak of sp^2 carbon in the $C_{2n}H_2$-filled SWCNTs has a redshift by 0.12 eV. The shift towards low binding energy implies the transfer of electrons from polyynes to SWCNTs, further confirming the $C_{2n}H_2$ has been successfully filled in the SWCNTs.

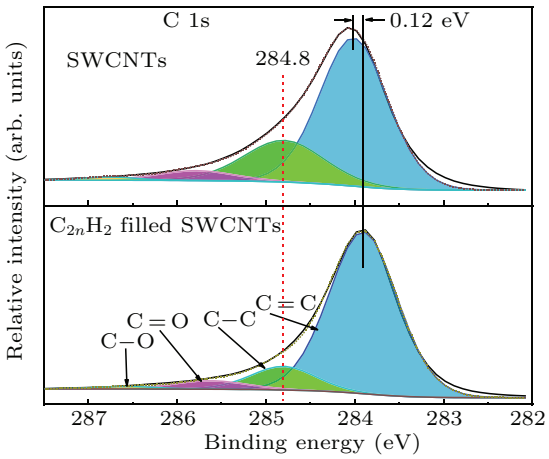


Fig. 5. High-resolution XPS spectra of C 1s for SWCNTs before and after being filled with $C_{2n}H_2$.

4. Conclusion and perspectives

In summary, we described a simple and low-cost method for the preparation of $C_{2n}H_2$ by laser marking machine to ablate graphite plate in liquid. Using this method, the polyynes, such as C_8H_2, $C_{10}H_2$, $C_{12}H_2$, and $C_{14}H_2$ can be quickly prepared on a large scale. Employing the fast-scanning capability of the laser marking machine, the destruction of polyynes resulting from local high temperature can be greatly avoided, which is essential for the preparation of polyynes in large quantities. Moreover, as long as the solution is kept at a low temperature, the kilowatt-level, high-power lasers will be utilized in the fabrication of polyynes in large quantities. Additionally, we use an *in-situ* Raman spectrometer to study the filling process of SWCNTs with these polyynes. All results show that $C_{2n}H_2$ can be fast filled into SWCNTs under laser irradiation. This provides a new idea for solving the transport problem of precursors in the preparing process of LLCCs by confinement reactions in one-dimensional channels of SWCNTs. Therefore, our reported preparation strategy of $C_{2n}H_2$ and the filling method of SWCNTs with $C_{2n}H_2$ will provide a new way to study the LLCCs in a confined space.

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References

[1] Whittaker A G and Kintner P L 1969 *Science* **165** 589
[2] Whittaker A and Kintner P 1969 *Science* **165** 589
[3] Zhao X, Ando Y, Liu Y, Jinno M and Suzuki T 2003 *Phys. Rev. Lett.* **90** 187401
[4] Liu M, Artyukhov V I, Lee H, Xu F and Yakobson B I 2013 *ACS Nano* **7** 10075
[5] Ming C, Meng F X, Chen X, Zhuang J and Ning X J 2014 *Carbon* **68** 487
[6] Tarakeshwar P, Buseck P R and Kroto H W 2016 *J. Phys. Chem. Lett.* **7** 1675
[7] Shi L, Sheng L, Yu L, An K, Ando Y and Zhao X 2011 *Nano Res.* **4** 759
[8] Zhao C, Kitaura R, Hara H, Irle S and Shinohara H 2011 *J. Phys. Chem. C* **115** 13166
[9] Sun Q, Cai L, Wang S, Widmer R, Ju H, Zhu J, Li L, He Y, Ruffieux P, Fasel R and Xu W 2016 *J. Am. Chem. Soc.* **138** 1106
[10] Shi L, Rohringer P, Suenaga K, Niimi Y, Kotakoski J, Meyer J C, Peterlik H, Wanko M, Cahangirov S, Rubio A, Lapin Z J, Novotny L, Ayala P and Pichler T 2016 *Nat. Mater.* **15** 634
[11] Zhang Y F, Zhao J W, Fang Y H, Liu Y and Zhao X L 2018 *Nanoscale* **10** 17824
[12] Chang W, Liu F, Liu Y, Zhu T, Fang L, Li Q, Liu Y and Zhao X 2021 *Carbon* **183** 571
[13] Taguchi Y, Endo H, Abe Y, Matsumoto J, Wakabayashi T, Kodama T, Achiba Y and Shiromaru H 2015 *Carbon* **94** 124
[14] Compagnini G, Mita V, Cataliotti R S, D'Urso L and Puglisi O 2007 *Carbon* **45** 2456
[15] Tabata H, Fujii M and Hayashi S 2006 *Carbon* **44** 522
[16] Cataldo F 2004 *Carbon* **42** 129
[17] Fang L, Zhu T, Chang W, Liu Y and Zhao X 2021 *Carbon* **179** 28
[18] Li Y, An K, Sheng L, Yu L, Ren W and Zhao X 2015 *Chem. Phys. Lett.* **631–632** 12
[19] Chalifoux W A and Tykwinski R R 2010 *Nat. Chem.* **2** 967
[20] Cataldo F (ed.) 2005 *Polyynes: Synthesis, Properties, and Applications* (CRC Press)
[21] Cataldo F 2005 *Carbon* **43** 2792
[22] Saito T, Ohshima S, Okazaki T, Ohmori S, Yumura M and Iijima S 2008 *J. Nanosci Nanotechnol.* **8** 6153
[23] Fang L, Sheng L, An K, Yu L, Ren W, Ando Y and Zhao X 2013 *Physica E* **50** 116
[24] Wu Z C, Chen Z H, Du X, Logan J M, Sippel J, Nikolou M, Kamaras K, Reynolds J R, Tanner D B, Hebard A F and Rinzler A G 2004 *Science* **305** 1273
[25] Tabata H, Fujii M, Hayashi S, Doi T and Wakabayashi T 2006 *Carbon* **44** 3168
[26] Zhang K, Zhang Y F and Shi L 2020 *Chin. Chem. Lett.* **31** 1746
[27] Shi L, Senga R, Suenaga K, Kataura H, Saito T, Paz A P, Rubio A, Ayala P and Pichler T 2021 *Nano Lett.* **21** 1096