Postprint

This is the accepted version of a paper published in *J. Am. Chem. Soc.*
This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Bottom-Up Synthesis of Metalated Carbyne

Qiang Sun[†], Liangliang Cai[†], Shiyong Wang[#], Roland Widmer[#], Huanxin Ju[‡], Junfa Zhu[‡], Lei Li[§], Yunbin He[§], Pascal Ruffieux[#], Roman Fasel[#, ‖] and Wei Xu*,[†]

[†]Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Caoan Road 4800, Shanghai 201804, P.R. China

[#]Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

[‡]National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, P.R. China

[§]Ministry-of-Education Key Laboratory of Green Preparation and Application for Functional Materials, Faculty of Materials Science & Engineering, Hubei University, Wuhan 430062, P.R. China

[‖]Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

ABSTRACT: Due to stability issues, carbyne, a one-dimensional chain of carbon atoms, has been much less investigated than other recent carbon allotropes such as graphene. Beyond that, metalation of such a linear carbon nanostructure with regularly distributed metal atoms is even more challenging. Here, through an on-surface synthesis approach, we report a successful on-surface synthesis of metalated carbyne chains by dehydrogenative coupling of ethyne molecules and copper atoms on a Cu(110) surface under ultrahigh vacuum conditions. The length of the fabricated metalated carbyne chains is found to extend into the submicron scale (with the longest ones up to ~120 nm). We expect that the herein developed on-surface synthesis strategy towards the efficient synthesis of organometallic carbon-based nanostructures will inspire more extensive experimental investigations on their physicochemical properties and explorations of their potential with respect to technological applications.
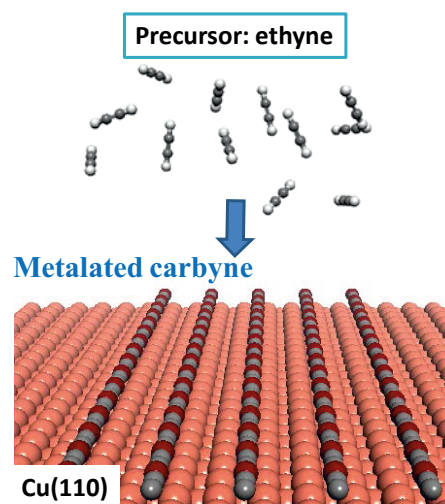
Figure 1. Illustration of the bottom-up synthesis of metalated carbyne on Cu(110). The ball-and-stick model shows the formation of metalated carbyne through dehydrogenative coupling of ethyne precursors and copper adatoms on Cu(110) under UHV conditions. Grey: carbon; white: hydrogen; brown: copper substrate atom; red: copper adatom.

For a long time, carbon-based materials have received tremendous attention, fueled also by the successive discoveries of novel carbon allotropes such as fullerenes, carbon nanotubes and graphene, which exhibit extraordinary properties rendering potential scientific and industrial applications[1]. Another carbon allotrope, carbyne - a linear, one-dimensional chain of carbon atoms - is also expected to have interesting properties such as extreme mechanical behaviors (i.e. ultra high stiffness and Young's modulus) of known materials[2], room-temperature superconductivity[3,4], intriguing non-linear optical properties[5] and high hydrogen storage capability[6]. Although the structure of carbyne has been proposed long time ago, the scientific advances made on carbyne are limited in comparison with other carbon allotropes, and the main challenge lies in synthesizing the elusive carbyne with well-defined structure[7-9]. Beyond that, metalation of such a carbon nanostructure with well-distributed metal atoms is even more challenging and of great interest, because it may allow to regulate the intrinsic physicochemical properties of the carbon nanostructure/nanomaterial[10,11].

Recently, on-surface synthesis has emerged as a rapidly developing research field due to its fascinating potential in the fabrication of novel nanostructures/nanomaterials. Among others, carbon nanomaterials like fullerenes[12], graphene[13,14], graphene nanoribbons[15] and single-chirality carbon nanotubes[16] have been achieved by such a method. Inspired from recent investigations of dehydrogenative/dehalogenated coupling of terminal alkynes/alkynyl bromides with metal atoms on surfaces[17,18], in this study, we chose the ethyne molecule (the simplest alkyne with two terminal alkynyl groups) as a precursor with the aim of forming linear metalated carbon chains through on-surface dehydrogenative coupling, as sketched in Figure 1. The anisotropic Cu(110) surface was selected because of its relatively high chemical activity and the well-known one-dimensional (1-D) templating effect that facilitates the formation of 1-D carbon-based nanomaterials. Herein, we show that we have successfully synthesized

metalated carbyne by a facile and highly efficient surface chemistry method. We report characterization of the products by high-resolution scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM) and X-ray photoelectron spectroscopy (XPS), combined with density functional theory (DFT) calculations. We find that the length of the obtained metalated carbyne chains extends into submicron range.
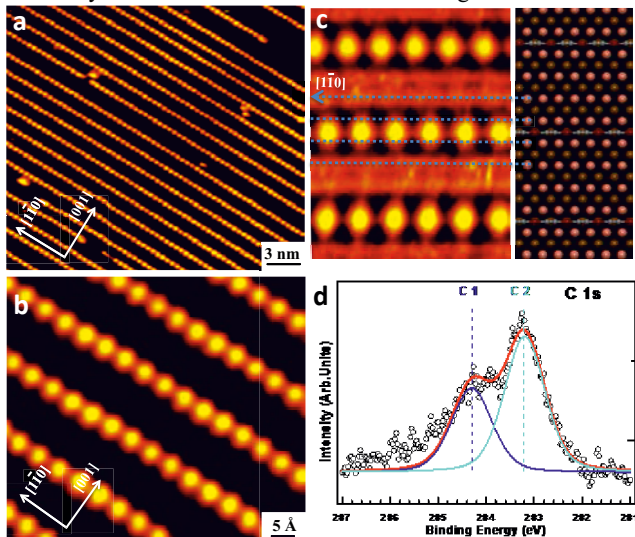

Figure 2. (a) Large-scale and (b) close-up STM images showing the formation of metalated carbyne chains. (c) High-resolution STM image resolving metalated carbyne and the substrate lattice simultaneously. The underlying copper rows along the [1-10] direction are indicated by blue dashed lines. The corresponding DFT-optimized structure model of metalated carbyne is presented aside for comparison. (d) C 1s core level XP spectrum showing the major peak C2 located at a binding energy of 283.2 eV (cyan curve).

After deposition of ethyne on Cu(110) at low temperatures (~220 K) and under ultrahigh vacuum conditions, we mainly find the formation of bright protrusions, which desorb from the surface after gentle annealing of the sample to ~330 K (Figure S1). These observations are in agreement with a previous study showing that ethyne could be cyclized into benzene on Cu(110), which was determined by temperature programmed desorption[19]. After deposition of ethyne at temperatures between RT and 400 K, we observe complicated structures (shown in Figure S2) whose nature could not be unambiguously determined. Some of them can be assigned to polyacetylene with the help of high-resolution nc-AFM imaging. Detailed structural and spectroscopic analysis are underway to elucidate these structures (the corresponding results will be reported elsewhere). Then, we try to optimize the experimental conditions by substrate temperature regulation to avoid undesired side reactions and to facilitate the dehydrogenative coupling reaction.
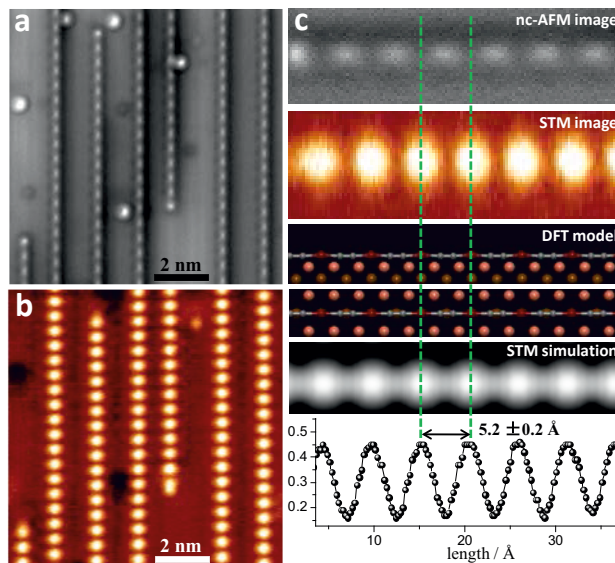

Figure 3. (a) Large-scale nc-AFM frequency shift image. The image is taken at constant-height mode using a CO terminated tip at a small bias voltage of 5 mV. (b) Current image acquired simultaneously with frequency shift image in (a). (c) Equally scaled high-resolution nc-AFM frequency shift image, current image, DFT optimized model, STM simulation and line-scan profile of a single metalated carbyne chain on Cu(110).

As shown in Figure 2a, after deposition of ethyne (with a base pressure of 1×10^{-8} mbar for 10 minutes) on the surface held at ~450 K, 1-D chains along the close-packed [1-10] direction of the substrate are formed. This chain structure is characterized by periodic protrusions in close-up STM images (Figure 2b). To get further insight, we have performed an X-ray photoelectron spectroscopy analysis. As depicted in Figure 2d, the C 1s spectrum shows a minor peak at ~284.3 eV (marked as C1) and a major peak at ~283.2 eV (marked as C2), respectively. According to previous experimental and theoretical studies, the peak at ~284.3 eV is characteristic of unsaturated carbon atoms on surfaces[15,20,21], and the lower-binding-energy (~283.2 eV) C 1s peak is attributed to carbon atoms bound to metal (copper atoms in this case)[20-23]. It is known that copper adatoms are often involved in dehydrogenative/dehalogenated coupling reactions by formation of organometallic species[17,24-26]. Therefore, we attribute this chain structure to metalated carbyne, i.e. [-Cu-C-C-]$_n$ 1D organometallic carbon chains. The high-resolution STM image shown in Figure 2c allows us to identify the registry between the metalated carbyne and the substrate lattice. We find that the metalated carbyne prefers to locate at the bridge sites of copper rows along the [1-10] direction, which is in good agreement with its theoretically optimized most stable structure (cf. right panel of Figure 2c). Given that the two carbon atoms within the metalated carbyne structure are equivalent, the C1 peak must be related to some other (undetermined) byproducts as indicated in Figure S3. It is noteworthy that we could easily fabricate well-defined metalated carbyne on the Cu(110) surface at different coverages. At relatively high coverage (~0.8 monolayer) the surface is predominately covered by metalated carbyne chains, the longest of which reaches to ~120 nm (Figure S4).

We believe that the substrate temperature plays a crucial role in facilitating the formation of metalated carbyne on Cu(110) based on the considerations as follows: i) the relatively high substrate temperatures (450 K in this case) provide enough thermal

energy for dehydrogenation of ethyne on the surface; ii) there are enough free copper adatoms existing at such a substrate temperature; and iii) a specific temperature window may prohibit unwanted side reactions and allow for selective triggering of the metal-assisted dehydrogenative coupling reaction. It has also been reported that upon post-annealing the Cu atoms could be released from the C-Cu-C structures and converted into purely C-C bonded structures[24]. We thus also post-annealed our metalated carbyne samples to 500 K, 550 K and 600 K gradually. Rather than the formation of C-C bond, however, we found a gradual decrease of the coverage of metalated carbyne, and finally the degradation of all carbon atoms. We have performed similar experiments on Ag(110) and Au(110) surfaces, but found that ethyne molecules would hardly stick on both surfaces in a wide temperature range ($T_{substrate}$ from 180 K to 600 K), indicating relatively weak interactions between ethyne and these two surfaces.
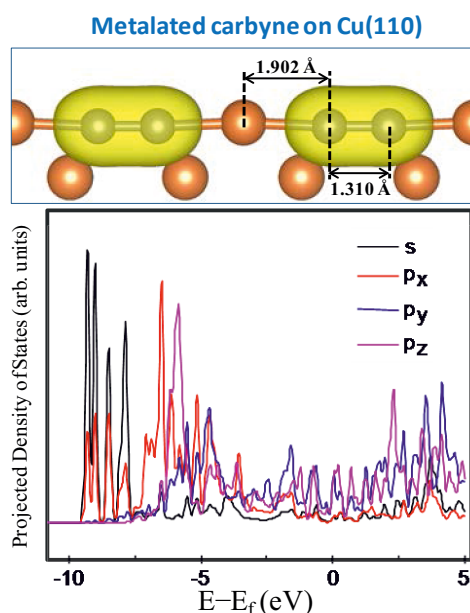

Figure 4. Top: DFT optimized model of metalated carbyne on Cu(110) and its electron densities (shown in yellow) at isosurface value of 0.4 e$Å^{-3}$. The lengths of the carbon-carbon and carbon-copper bonds are indicated. Bottom: Corresponding PDOS on the s, p_x, p_y and p_z orbitals of the carbon atoms of metalated carbyne on Cu(110).

To further verify the formation of metalated carbyne and unravel its atomic scale structure, we have resorted to nc-AFM imaging in conjunction with extensive DFT calculations. As shown in Figure 3a,b the simultaneously acquired nc-AFM frequency shift and current images show the same characteristic chain structure as the one depicted in Figure 2, which undoubtedly confirms the proposed metalated carbyne structure on the surface. From a comparison of the equally scaled high-resolution nc-AFM frequency shift image, STM image (i.e. current image), DFT optimized model, STM simulation and lines-can profile of a metalated carbyne chain on Cu(110), as shown in Figure 3c, we determine that i) the experimental periodicity of the metalated carbyne chain is 5.2 ± 0.2 Å which corresponds to two copper lattice spacings along the [1-10] direction; ii) the periodic protrusions of the chain seen in the STM images are attributed to the incorporated copper atoms; and iii) the copper atoms are not imaged in the nc-AFM imaging, instead, the carbon-carbon bonds are resolved.

To elucidate this at first sight unexpected phenomenon we performed further DFT calculations to analyze the electronic properties of a metalated carbyne chain on Cu(110). As shown in Figure 4, the corresponding electron density and bond length analyses clearly reveal the alternating carbon-carbon (1.310 Å) and carbon-copper (1.902 Å) bonds. Moreover, it is clearly seen that high electron densities mainly locate along the carbon-carbon bonds, which accounts for the bright protrusions being the carbon-carbon bonds reflected in the nc-AFM imaging. The projected density of states (PDOS) of the carbon atoms demonstrates the sp hybridization characteristics, as reflected from the overlapping of the electronic features of s and p_x orbitals, and the interaction between carbon atoms and copper atoms is reflected in a broadening of the electronic features of p_y and p_z orbitals.

Synthesis of well-defined metalated carbon nanostructures has remained as a major experimental challenge due to the difficulty in incorporating metal atoms into carbon scaffolds. To the best of our knowledge, metalated carbyne structures have not been achieved before. In our study, the anisotropic Cu(110) substrate not only serves as a catalytically active template for directing the growth of unidirectional metalated carbyne chains but also separates them from each other because of their energetically favorable bridge adsorption sites, which inhibits the occurrence of cross-linking.

The present on-surface chemistry strategy demonstrates a facile and highly efficient method to fabricate metalated carbyne, which paves the way to further explorations of its properties and potential applications. The involvement of metal atoms provides a versatile manner for modulating the intrinsic electronic properties of carbon nanostructures, which will perspectively enrich their potential applications in diverse fields. For example, metal-doped carbon nanomaterials could be promising for organic superconductors[10,11]. A further challenging objective will be to explore the feasibility of transferring the synthesized metalated carbyne outside UHV conditions by methods similar to the ones developed for epitaxial graphene[27].

ASSOCIATED CONTENT

Supporting Information

Experimental details and additional STM images. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

xuwei@tongji.edu.cn (W.X.)

Notes

The authors declare no competing financial interests.

REFERENCES

[1]   Hirsch, A. *Nat. Mater.* **2010**, *9*, 868–871.

[2]   Liu, M.; Artyukhov, V. I.; Lee, H.; Xu, F.; Yakobson, B. I. *ACS Nano* **2013**, *7*, 10075–20082.

[3]   Heimann, R. B.; Kleiman, J.; Salansky, N. M. *Nature* **1983**, *306*, 164–167.

[4]   Little, W. A. *Phys. Rev.* **1964**, *134*, 1416–1424.

[5]   Eisler, S.; Slepkov, A. D.; Elliott, E.; Luu, T.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2666–2676.

[6]   Sorokin, P. B.; Lee, H.; Antipina, L. Y.; Singh, A. K.; Yakobson, B. I. *Nano Lett.* **2011**, *11*, 2660–2665.

[7]   Chalifoux, W. A.; Tykwinski, R. R. *Nat. Chem.* **2010**, *2*, 967–971.

[8]   Zhao, X.; Ando, Y.; Liu, Y.; Jinno, M.; Suzuki, T. *Phys. Rev. Lett.* **2003**, *90*, 187401.

[9]   Hayatsu, R.; Scott, R. G.; Studier, M. H.; Lewis, R. S.; Anders, E. *Science* **1980**, *209*, 1515–1518.

[10]   Wang, X. F.; Liu, R. H.; Gui, Z.; Xie, Y. L.; Yan, Y. J.; Ying, J. J.; Luo, X. G.; Chen, X. H. *Nat. Commun.* **2011**, *2*, 507.

[11]   Hebard, A.; Rosseinky, M.; Haddon, R.; Murphy, D.; Glarum, S.; Palstra, T.; Ramirez, A.; Karton, A. *Nature* **1991**, *350*, 600–601.

[12]   Otero, G.; Biddau, G.; Sánchez-Sánchez, C.; Caillard, R.; López, M. F.; Rogero, C.; Palomares, F. J.; Cabello, N.; Basanta, M. A.; Ortega, J.; Méndez, J.; Echavarren, A. M.; Pérez, R.; Gómez-Lor, B. Martín-Gago, J. A. *Nature* **2008**, *454*, 865–868.

[13]   Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Vela-makanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, 1312–1314.

[14]   Treier, M.; Pignedoli, C. A.; Laino, T.; Rieger, R.; Müllen, K.; Passerone, D.; Fasel, R. *Nat. Chem.* **2011**, *3*, 61–67.

[15]   Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R. *Nature* **2010**, *466*, 470–473.

[16]   Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel. R. *Nature* **2014**, *512*, 61–64.

[17]   Liu, J.; Chen, Q.; Xiao, L.; Shang, J.; Zhou, X.; Zhang, Y.; Wang, Y.; Shao, X.; Li, J.; Chen, W.; Xu, G. Q.; Tang, H.; Zhao, D.; Wu, K. *ACS Nano* **2015**, *9*, 6305–6314.

[18]   Unpublished work.

[19]   Lomas, J. R.; Baddeley, C. J.; Tikhov, M. S.; Lambert, R. M. *Langmuir* **1995**, *11*, 3048–3053.

[20]   Zhang, Y. Q.; Kepčija, N.; Kleinschrodt, M.; Diller, K.; Fischer, S.; Papageorgiou, A. C.; Allegretti, F.; Björk, J.; Klyatskaya, S.; Klappenberger, F.; Ruben, M.; Barth, J. V. *Nat. Commun.* **2012**, *3*, 1286.

[21]   Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Revurat, Y. F.; Cossaro, A.; Verdini, A.; Perepichka, D. F.; Rosei, F.; Contini, G. *ACS Nano* **2013**, *7*, 8190–8198.

[22]   Bushell, J.; Carley, A. F.; Coughlin, M.; Davies, P. R.; Edwards, D.; Morgan, D. J.; Parsons, M. *J. Phys. Chem. B* **2005**, *109*, 9556–9566.

[23]   Bjork, J.; Hanke, F.; Stafstrom, S. *J. Am. Chem. Soc.* **2013**, *135*, 5768–5775.

[24]   Wang, W.; Shi, X.; Wang, S.; Van Hove, M. A.; Lin, N. *J. Am. Chem. Soc.* **2011**, *133*, 13264–13267.

[25]   Haq, S.; Hanke, F.; Dyer, M. S.; Persson, M.; Iavicoli, P.; Amabilino, D. B.; Raval, R. *J. Am. Chem. Soc.* **2011**, *133*, 12031–12039.

[26]   Zhang, C.; Sun, Q.; Chen, H.; Tan, Q.; Xu, W. *Chem. Commun.* **2015**, *51*, 495–498.

[27]   Lee, Y.; Bae, S.; Jang, H.; Jang, S.; Zhu, S. E.; Sim, S. H.; Song, Y. Il; Hee Hong, B.; Ahn, J. H. *Nano Lett.* **2010**, *10*, 490–493.

TOC Graphic